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THE EFFECT OF LEAD OXIDE POWDER

ON BATTERY PASTE COMPOSITION

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## ABSTRACT

### THE EFFECT OF LEAD OXIDE POWDER ON BATTERY PASTE COMPOSITION

The aim of the research was to determine the effect of ball mill produced lead oxide powder on freshly produced positive paste. This knowledge would enable the company to manufacture positive electrodes with consistent composition for use in sealed, valve regulated, lead (Pb)/sulphuric acid ( $H_2SO_4$ ) batteries.

Positive battery paste is predominantly composed of lead oxide powder. The company considered that the composition of freshly mixed positive paste was dependant on the quality of lead oxide powder. However, this investigation of lead oxide quality variations has revealed no clear correlation with paste density fluctuations.

Before tests could commence to assess the effect of lead oxide quality on positive paste composition, an explanation for previous lead oxide quality variations and the lack of correlation with positive paste density had to be determined. The variations in lead oxide quality were assumed to be the result of either the analytical errors associated with the test procedures used to assess quality by the oxide mill operators or ball mill process variables varying unnoticed. Both hypotheses were extensively studied and it was determined that measurement errors were the main problem. An alternative analysis technique, referred to as the acetic acid method, was introduced to solve the problem.

Once the reason for the lack of correlation between lead oxide quality and positive paste composition had been determined, the effect of lead oxide quality on paste composition was determined. A series of tests referred to as fractional factorial optimisation tests were performed using various batches of lead oxide powder. The composition of each trial positive paste mix was assessed. Through the use of regular analysis techniques, the characteristic lead oxide required to produce a positive paste with a well defined narrow density range was determined and the ball mill process was set up to produce only the required type of oxide.

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## CHAPTER ONE

### 1.0 INTRODUCTION<sup>1</sup>

A Teaching Company Scheme Research Programme was carried out between Yuasa Battery (U.K.) Limited and the University of Glamorgan. The Project's aim was to enable the company to batch produce battery paste with a consistent composition for use in sealed lead (Pb)/ sulphuric acid ( $H_2SO_4$ ) battery manufacture.

Paste forms the chemical basis of the battery electrodes. The battery electrode material is referred to as active material. There are two types of battery paste. Positive paste is used to produce positive battery electrodes, whereas negative paste produces negative battery electrodes. The role of the paste is to produce active material with sufficient porosity, rigidity and cohesion to withstand vibration in service, as well as the dimensional changes that occur on charging and discharging. It is believed that variations in paste composition effect both battery performance and lifetime.

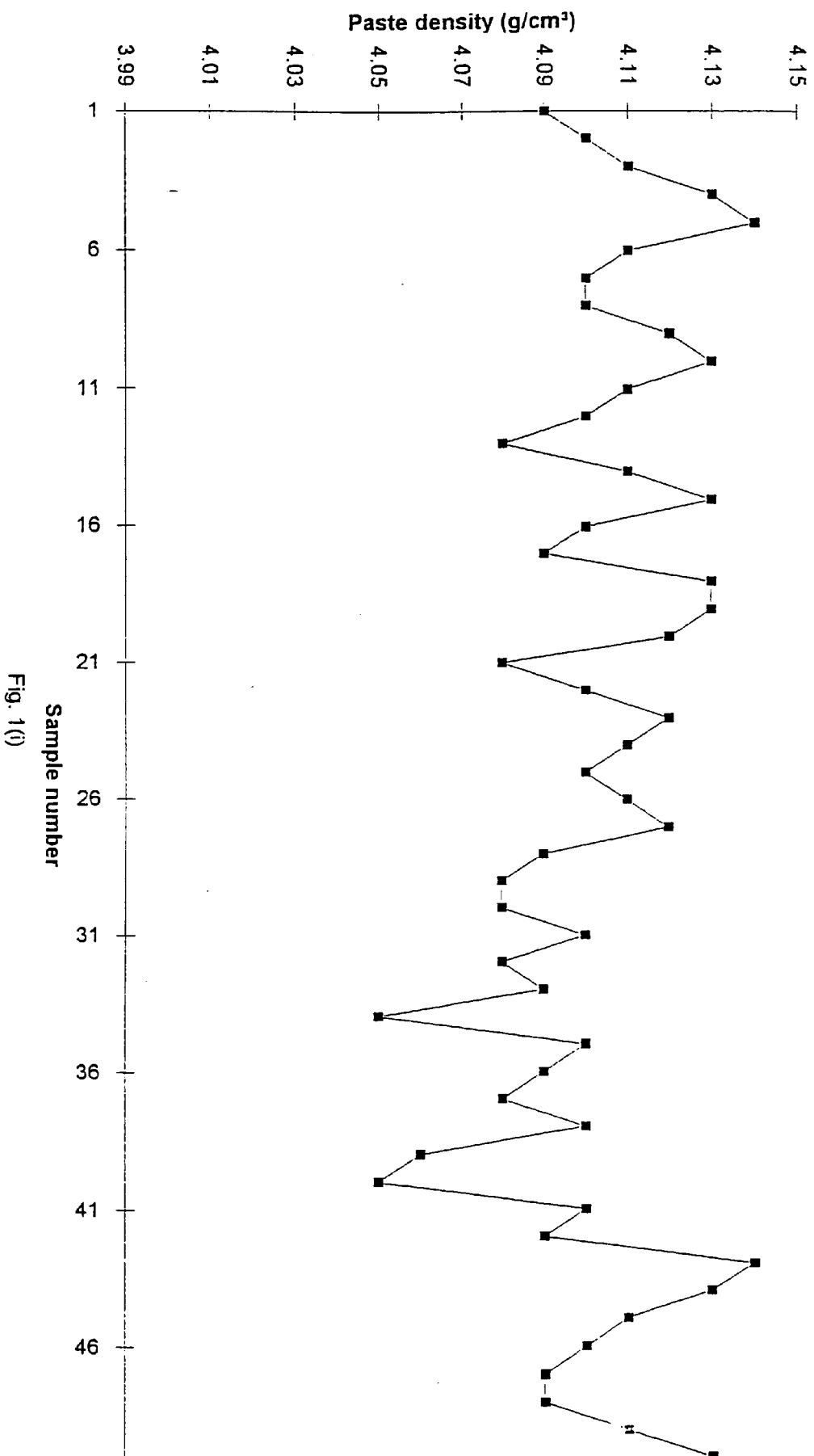
The company uses a batch mixing process to produce battery paste. The composition is measured immediately after a paste has been mixed. Battery

paste has the similar physical characteristics of general pastes and these can therefore be used to assess composition, i.e. density and particle surface area. The property chosen to measure paste composition is density. This property has a recommended specification range and if density values for each paste batch are within it, the paste is assumed to be of the necessary composition for use in battery electrode production. For positive paste, the specification range is from 4.00 g/cm<sup>3</sup> to 4.20 g/cm<sup>3</sup> and for negative paste from 4.20 g/cm<sup>3</sup> to 4.40 g/cm<sup>3</sup>. Density is measured off-line and the experimental procedure is capable of reproducible results.

Figure 1(i) shows the densities of each batch of positive paste mixed over a period of one week, ten density measurements are performed each day. The density variation over each day was approximately  $\pm 0.05$  g/cm<sup>3</sup>, whereas the variation for the week is  $\pm 0.10$  g/cm<sup>3</sup>.

Although Figure 1(i) reveals that all the paste densities were within specification, the company was not happy with the range of results. The company believed that slight variations in positive paste composition could lead to variations in both battery performance and lifetime properties.

Figure 1 (i) Variation in density measurements performed on freshly mixed positive pastes



For each mixed batch of positive paste, calculated ingredient weights and a set mixing time have been used to ensure that a paste density of  $4.10 \text{ g/cm}^3$  can be obtained. Over many years of producing and testing sealed lead sulphuric acid batteries the company believe that batteries which give excellent performance and last their specified lifetime have positive electrodes made with paste having a density of  $4.10 \text{ g/cm}^3$  ( $\pm 0.01 \text{ g/cm}^3$ ).

However the results in Figure 1(i) clearly reveal that they were unable consistently to produce batches of positive paste with this density. As a result, the company was very worried about the quality of positive electrodes they produced. The exact density of negative pastes is not so critical. As long as it is within specification, good quality negative electrodes will be produced.

Because of the problems the company had trying consistently to produce positive paste with a density of  $4.10 \text{ g/cm}^3$ , the paste ingredients and the mixing process were investigated to assess what could be the cause of the variations. It was obvious that accurately weighing and mixing of the paste ingredients was not sufficient enough to ensure the production of paste with a consistent density. There was some other factor affecting the paste

composition. The senior technical staff at the company believed that the composition variations were the result of variations in quality of one of the paste ingredients. The key ingredient is lead oxide (PbO) powder which was also manufactured at the company's site and is the major component of battery paste.

#### THE FACTORS RESPONSIBLE FOR THE VARIATION IN PASTE COMPOSITION

Positive battery paste is produced by mixing lead oxide powder, 1.4 specific gravity sulphuric acid, water and polypropylene fibres. For negative pastes two additional additives are required. These are sodium lignosulphonate and barium sulphate (known as expanders). Negative pastes require expanders because they help the electrochemical discharge reactions to proceed more smoothly. Paste is produced in "500 kilogram" (kg) batches. The quantities of each component are lead oxide (500 kg), sulphuric acid (65 kg), water (65 litres) and polypropylene fibres (150 g). For negative pastes sodium lignosulphonate (6 kg) and barium sulphate (1 kg) are also added.

Lead oxide is produced from the tumbling action of lead pellets in a cylindrical mill through which an

airstream is passed. This process is referred to as the ball mill method for producing lead oxide powder. The powder is produced containing the beta polymorphic form of lead oxide along with small traces of un-oxidised lead (referred to as the free lead content).

The quality of freshly produced ball mill lead oxide powder is tested every two hours by the process operators. Two characteristic properties of the fresh powder are used to represent its quality. Each property has a recommended specification range and if results are within the limits, the powder can be considered acceptable for paste production. The operators use the quality results to control the ball mill process manually, by adjusting certain ball mill process variables to ensure lead oxide quality remains within the specification.

The other components in battery paste are not manufactured on site but are bought in. However, before being used in pasting, the company's Quality Assurance Laboratory has to approve each batch. If component quality is within the manufacturers' specification, it can be accepted for use in production.

It is the belief of the company's technical staff



that a particular lead oxide quality could be responsible for a particular paste composition. That is, to consistently achieve a paste density of  $4.10 \text{ g/cm}^3$  requires a consistent lead oxide powder. Hence if lead oxide quality is continually varying, batches of paste will be produced with fluctuating densities. It therefore appears that the factor which could be influencing the composition of freshly mixed paste is some unmeasured parameter of the lead oxide powder being used.

Before discussing the possible variations in the quality of freshly produced lead oxide powder and the possible correlation with the fluctuations in paste composition, it is first necessary to introduce the important role lead oxide powder plays in the production of battery electrode active material.

## 1.2 THE MANUFACTURE OF ACTIVE MATERIAL FOR POSITIVE AND NEGATIVE ELECTRODES

Figure 1(ii) represents each stage of active material production.

Figure 1(ii) The steps involved in the preparation of battery electrodes

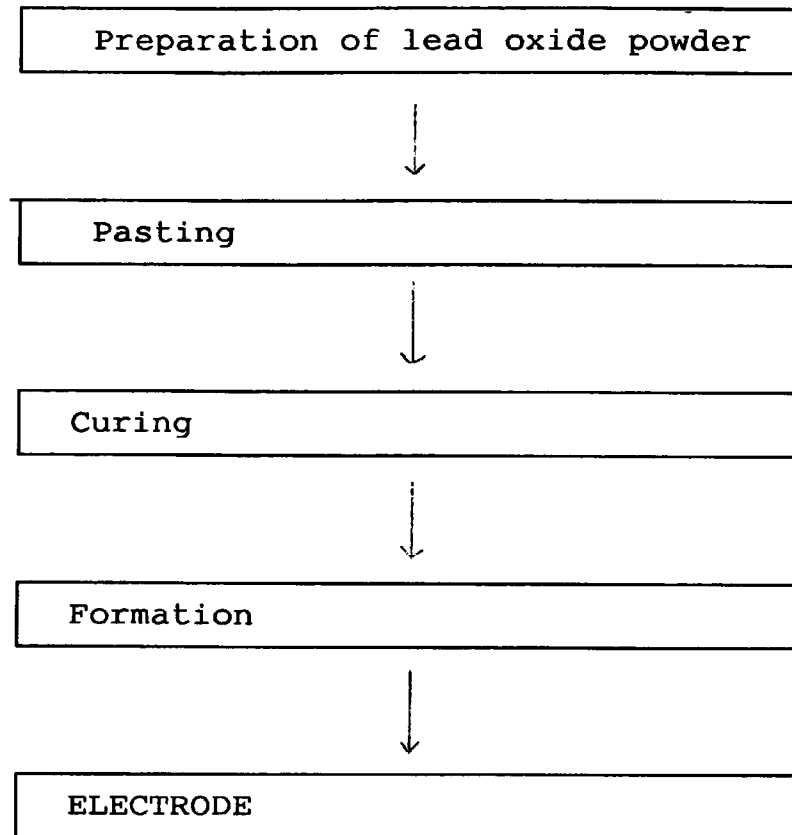


Figure 1(ii)

1.2.1 Preparation of lead oxide powder<sup>2,9</sup>

In the early years of lead/acid battery manufacturing two types of lead oxide were used. These were:

- (i) litharge ( $\text{PbO}$ ); and
- (ii) red lead ( $\text{Pb}_3\text{O}_4$ ).

The production of litharge involved the reaction of molten lead with controlled air and reaction temperature. Under these conditions yellow or red/yellow crystals of lead oxide were produced. Red lead was produced by heating litharge under controlled conditions. Red lead contains approximately 65 to 70%  $\text{Pb}_3\text{O}_4$  and the rest  $\text{PbO}$ .

Both red lead and litharge contained only small residual content of free lead because, at the time, battery companies believed it lowered the final porosity of the battery electrodes. The early battery manufacturers produced positive paste using equal quantities of red lead and litharge, whereas negative paste contained only litharge. The use of these types of lead oxides in paste production persisted until the 1930's.

During the late 1930's a new type of lead oxide for battery manufacturing began to be produced. It contained approximately 30% free lead with the remaining material being  $\text{PbO}$ . In early production runs, 50% free lead remained and, because of its colour, it became known as black oxide. It is also known as leady or grey oxide.

The development of this type of lead oxide enabled battery manufacturers to eliminate the more expensive

red lead from positive paste. This step produced a cost saving and simplified positive paste production. As a result of the introduction of this new lead oxide, battery manufacturers became aware of the purchase cost. In a bid to cut costs, companies developed their own methods of production. In the early 1940's the first rotating mill for lead oxide production came into operation.

Also at this time, the lead oxide manufacturers, realising that they could be losing trade, offered a variety of lead oxide types. These types of lead oxide are produced by a process known as the Barton pot method.

Today a number of different lead oxides are used. The easiest way to classify them is according to their method of manufacture. Although the various lead oxides can be prepared by wet chemical methods, all significant production is performed using direct oxidation of lead with air. The different processes are classified according to the temperature of reaction.

#### 1.2.1.1 Low temperature processes

(Below the melting point of lead)

The only low temperature thermal process is ball milling. It involves lead pellets being rotated in a cylindrical mill through which an airstream is passed. The heat which is generated through the tumbling action of the pellets is enough to start the exothermic oxidation process.

#### 1.2.1.2 Moderate temperature processes

(Between the melting point of lead and that of lead oxide)

There are three quite different moderate temperature processes. These are:-

##### (i) Mechanical Furnace

This is a batch process which consists of a cast steel pan installed in a refractory furnace. The pan is charged with molten lead which is kept moving. Inside the pan a stirring mechanism constantly exposes a fresh surface of molten lead for oxidation. In the floor of the pan a port expels the charge into a conveyor where it is heated by a gas flame. The lead oxide produced contains traces of both  $Pb_3O_4$  and free lead. The beta polymorphic form of

PbO is produced (the beta form has an orthorhombic crystal structure).

(ii) Rotary Tube Furnace

This is a continuous process which involves spraying molten lead into the higher end of an inclined tube lined with refractory material. At the other end of the tube, a gas flame maintains the desired temperature. The lead oxide produced contains traces of  $\text{Pb}_3\text{O}_4$  and free lead. The beta polymorphic form of PbO is produced.

(iii) Barton Pot Process

This is one of the most popular methods for producing lead oxide in the battery industry. A cast iron pot contains stirrers, both at the top and bottom. These rotate at different speeds. Molten lead is passed into the pot through a hole in the cover lid. The fast rotating top stirrers break up the molten lead into droplets which are oxidised and swept out of the top by an airstream. The lower stirrers operate at low speeds and keep

the droplets which avoid oxidation in motion. The oxidation reaction provides enough heat to keep the reaction in progress. The lead oxide produced contains the beta form of PbO and traces of free lead. However, it is also possible to have traces of the alpha PbO (the alpha form has a tetragonal crystal structure).

#### 1.2.1.3 High temperature processes

(Above the melting point of lead oxide)

There are two high temperature processes:-

##### (i) Fused Litharge Furnace

The fused litharge furnace consists of a reaction bath with a large iron water jacket which is lined with refractory bricks. Molten lead oxide is tapped off over a water cooled dam into cast iron pots, where it is allowed to cool. The beta form of lead oxide is produced. This process is no longer used because of the corrosive behaviour of molten lead and lead oxide in the reaction bath.

(ii) Fume Type Process

This process involves burning lead in a special type of blast burner with high pressure gas and air to give a very high temperature flame (approximately 1300 degrees centigrade). The oxidation occurs in a reaction chamber which can be either stationary or rotary. The product is a "smoke" and is removed from the reaction chamber by an airstream. The lead oxide produced by this method is referred to as "fumed" or "sublimed" product. The beta form of lead oxide is produced.

THE PROCESS OF LEAD OXIDE PRODUCTION AT YUASA BATTERY  
(U.K.) LIMITED

The low temperature thermal process of ball milling is used. This is a continuous process and the lead oxide which is produced is referred to as "ball mill oxide". The process involves lead pellets (each 50 g in weight) tumbling in a rotating drum through which a stream of air is passed. Under these conditions lead is oxidised. The heat which is generated through the tumbling action of the lead and the oxidation of lead abrasions in the airstream is sufficient to raise the temperature of the mill charge (lead in the ball mill) above the melting



point of lead. To prevent this from occurring, the steel drum of the ball mill is cooled. Water sprinklers over the external surface of the drum and a fan to remove hot air provides the cooling system.

The principle of operation of ball milling may appear simple and easy to control, but to manufacture a uniform product at a good production rate requires close attention to detail.

To ensure that consistent lead oxide is produced, two quality tests are performed every two hours. Each property has a recommended specification range. If results start to approach either the low or high specification limits, the process conditions are adjusted in order to return the property to the middle of the specification range.

The process variables which are monitored and controlled are:

- (i) air flow through the process;
- (ii) the ball mill temperature;
- (iii) the level (quantity) of ball mill charge.

Only one process variable is adjusted at a time and

as a result the process variables are used in a hierarchical fashion.

For example, the first variable which the process operators use to remedy the situation is the air flow through the process. If on analysis of further samples no change in properties is observed, the operators then adjust the process temperature. If adjusting both air flow and temperature has had no effect on consistency, the level of mill charge is altered as a last resort.

Lead oxide is removed from the ball mill by the airstream. This carries lead oxide from the ball mill to the filtering cyclones. The lead oxide produced contains the alpha form of PbO and 20 to 30% free lead.

#### 1.2.2 Pasting<sup>10-13</sup>

##### THE PASTING PROCESS AT YUASA BATTERY (U.K.) LIMITED

In the production of both types of paste, all components are mixed for approximately fifteen minutes in large on line pasting machines. The mixing process is separated into three stages. The first stage involves a dry mix of lead oxide and polypropylene fibres for one minute. For negative

mixes, both sodium lignosulphonate and barium sulphate are also present. The second stage is referred to as the wet mix. Water is added to the dry mix. The third stage involves the introduction of sulphuric acid over a period of six minutes. The resulting mixture, on addition of acid, changes from a stiff powder/water mixture to a pasty sulphate. The water in the mixture provides the role of a pore forming agent, whereas sulphuric acid provides the basic sulphates, which cause the necessary cementation reactions. Battery paste may be considered to be solid particles held together by capillary forces in a liquid.

The paste temperature during mixing has to be controlled. Both air cooling over the paste surface and the use of a water jacket around the mixing bowl, ensures that paste temperature remains below 50 degrees centigrade. Temperature is controlled because if allowed to increase, too much water will be lost, therefore increasing paste density. This could lead to problems in the later stages of electrode production.

During the mixing process, a complex mixture of compounds is formed, notably monobasic lead sulphate ( $\text{PbO.PbSO}_4$ ) and hydrated tribasic sulphate ( $3\text{PbO.PbSO}_4.\text{H}_2\text{O}$ ). In some cases the tetra basic

sulphate ( $4\text{PbO} \cdot \text{PbSO}_4$ ) is formed instead of the tribasic sulphate. The tetrabasic sulphate is formed at high paste temperatures. The tri- and tetrabasic sulphates are extremely important as their crystal features help to determine the rigidity and strength of the active materials.

The chemical reactions that occur during mixing are exothermic. This results in the temperature rising which causes evaporation of water. On completion of the mixing process, the pH of the paste has to be around 9 to 10 and the percentage of the free lead drops from approximately 20 - 28% to 10 - 12%. Once the mixing process has stopped, the paste density test is performed. If the results are within the recommended specification range, the paste is used for subsequent processing. However, if the results are not within specification, mixing continues for a short period of time until density values are within specification.

The battery paste is applied to cast lead alloy grids. These have been designed so that the grid lattice serves two functions:-

- (i) it supports the active material physically;

- (ii) it serves as the current collector to transfer electrons from the chemical reactions to the cell terminals.

Flat bed horizontal pasting machines are used to apply paste to the grids. Grids are carried on a moving belt that passes under a hopper containing paste. The hopper contains two rotating twin blades which force paste into the grids. A smoothing knife, positioned after the hopper, ensures that each grid is uniformly filled (it also controls the thickness of pasted grids).

The pasted grids move along to the end of the pasting belt where they drop onto a chain conveyor. Supporting lugs on the grid castings help carry them through high temperature gas ovens (set at 300 degrees centigrade). This is known as flash drying. The pasted grids are only subjected to a few minutes exposure to the ovens, so that just enough moisture can be removed (1 to 2%) in order that they can be stacked together without sticking. The flash dried grids are inserted into racks. Each rack contains ten rows of 150 grids.

The next stage in producing active material involves placing the racks of pasted grids into curing ovens to allow the setting process to develop.

### 1.2.3 Curing<sup>14</sup>

The earliest technique of curing pasted grids simply involved stacking grids on pallets and allowing them to dry. However, variations in results were obtained due to there being no control over ambient conditions.

To prevent variations in ambient conditions, areas in manufacturing plants are set aside. Pallets of pasted grids may be covered with canvas which minimises the effects of external weather conditions. The majority of battery manufacturing plants (including Yuasa Battery (U.K.) Limited) have expanded this concept by building rooms with heaters and humidity controls. The curing oven at Yuasa Battery (U.K.) Limited has a relative humidity of 85% and a temperature of 35 degrees centigrade.

In the curing ovens, pasted grids undergo a chemical process involving the free lead and oxygen, which is known as the hydroset process. The chemical combination is an exothermic reaction that requires a water catalyst<sup>14</sup>.

The tendency of the free lead/oxygen reaction to generate heat causes the entire pasted grid and the water present in it to heat up. As a result, surface

water will vaporise and bulk water migrates to the plate surface. The humidified atmosphere prevents too rapid water loss from the pasted grids (the humidified air maintains the water content in the paste). The initial water content in pasted plates entering the oven is approximately 10 to 12%. On completion of curing, the water content is approximately 4 to 5%. The reason for controlling the oven at 35 degrees centigrade is to ensure that the correct basic lead sulphate compounds are produced.

A feature of the reaction during curing, is that paste shrinkage occurs which results in paste contracting. There are two stages to this reaction:-

- (i) A steady loss of water and decrease in volume occurs. A certain amount of recrystallisation and oxidation of a small amount of free lead occurs producing a change from low porosity (large particle sizes) to high porosity (low particle sizes).
- (ii) This stage involves water removal with no further changes in volume. Water can only be removed when the voids have formed. No changes in porosity occur.

These features of cured pasted grids are important for the final porosity and the performance characteristics of the electrodes. Upon completion of the curing process (three days for positive pasted grids and two days for negatives), cured grids should be crack free and have a free lead of less than 1.5%. The grids are dried at a temperature of 100 degrees centigrade for twenty-four hours before being transferred to the formation tanks.

#### 1.2.4 Formation<sup>15</sup>

In formation tanks, the active material is finally produced. Positive grids are oxidised to lead dioxide ( $\text{PbO}_2$ ) and negative grids are reduced to spongy lead. In formation, the dried cured grids are electrochemically converted into fully charged active material. There are two methods which lead acid battery manufacturers can use. Both are employed by Yuasa Battery (U.K.) Limited.

##### (i) Tank Formation

In tank formation, positive dried pasted grids are connected in parallel, as are the negative grids, and placed in large baths containing sulphuric acid ranging from 1.0 to 1.1 specific gravity. Large



lead/acid battery factories can have up to twenty formation tanks connected in series.

Completion of formation is indicated by the colour of the grids. The positives are dark maroon, whilst negatives are light grey, with a metallic texture.

On completion of the formation reaction, the grids are lifted from the baths and allowed to drain before being dried in steam heated ovens at 100 degrees centigrade. After this stage, dried positive material contains at least 75%  $\text{PbO}_2$  with less than 5% lead sulphate ( $\text{PbSO}_4$ ). The highly reactive negative active material is oxidised in this drying process to form  $\text{PbO}$  which is converted into lead sulphate when assembled batteries are first primed with electrolyte.

(ii) Case Formation

This method involves forming dried cured pasted grids in the battery cases (The grids are cut into plates). The plates

are inserted into battery cases and sulphuric acid electrolyte is added. There is a twenty minute standing period to allow the acid to diffuse into the dried material. Each case is connected in series to a D.C. power supply. During formation, the battery cases have to be cooled in water baths.

The original case formation process involved two stages. The initial filling acid is replaced with fresh electrolyte because it contains impurities leached out by the forming reaction. Since handling operations are time consuming and costly and material specification is so much better, a single stage process is now used.

Successful completion of each stage results in active material possessing a porous structure. This consists of a framework of solid which is transected by a system of three dimensional interconnected capillaries that are uniformly distributed throughout the mass. This structure, which is built up from the initially loose lead oxide powder

possesses a certain stability, known as dry strength. The active material requires this to withstand the subsequent charge and discharging cycles it is subjected to.

In a very simplified form, lead acid batteries consist of a series of lead alloy grids impregnated with active material. Some of these are positive electrodes and others are negative electrodes. All are immersed in dilute sulphuric acid. This is the electrolyte, but it is also technically an active material because it takes part in the electrochemical reactions.

### 1.3 LEAD OXIDE QUALITY VARIATIONS

The two properties free lead and apparent density are used to measure the quality of freshly produced lead oxide powder. Both the quality and oxide mill process variables are monitored throughout production. The results of the quality measurements are used to control lead oxide production. For example, if test results start to approach the limits of the recommended specification range, one of the oxide mill process variables is adjusted in order to

return quality to the middle of the specification range. The quality tests are performed every two hours.

#### 1.4

#### THE TESTS USED TO MEASURE LEAD OXIDE QUALITY

There are two tests:

(i) Free lead determination

The experimental procedure involves dissolving a lead oxide sample in buffer solution and titrating the resulting mixture with ethylene diamine tetraacetic acid (E.D.T.A). Free lead is considered an important property to monitor and control because of the role it plays during pasting and the subsequent stages of active material manufacture. The role of free lead during the production of active material can be thought of as one of providing an energy source via its own oxidation, which allows the growth of certain crystalline compounds which are capable of forming rigid interlacing fibrous materials. The recommended specification range is 20 to 28%.

(ii) Apparent Density

The experimental procedure involves a sample being sieved through a mesh housed in a funnel. The sample is collected in a pre-weighed empty vessel. When full, the vessel is weighed and the apparent density of the powder is calculated. The recommended specification range is 0.95 to 1.25 g/cm<sup>3</sup>. Apparent density is an important property to monitor and control due to the important role it has during the formation of active material. It provides an estimate of the particle size distribution and porosity which have an affect on the reactions that take place during pasting.

The particle size distributions determine the internal surface area of the active material. Lead oxide powder with low apparent density is a result of particles not packing closely and implies that the particles are large and the powder is of low porosity. High apparent density powders are a result of small particles which results in high porosity. Battery manufacturers prefer to use a low porosity

lead oxide powder, as during the pasting process a change to higher porosity occurs.

Both the free lead content and apparent density tests are performed off line (each measurement requires a sample to be taken from the oxide mills and analysis is performed some time later).

Lead oxide has a number of other measurable properties which also have the potential to be used on or off-line. The two currently used tests mentioned above are the most convenient methods for assessing the quality of freshly produced lead oxide on the shop floor. Sophisticated laboratory equipment is required to be able to measure several of the other properties.

#### 1.5 ANALYSIS OF THE VARIATIONS IN LEAD OXIDE QUALITY

Figure 1(iii) represents a typical variation of free lead percentage. Analysis of the results has revealed considerable variation. All tests were performed by the process operator. The lead oxide produced during the week in question was used to

produce the paste batches whose densities are shown in Figure 1(i). Comparison of the free lead data (Figure 1(iii)) with the paste density data (Figure 1(i)) revealed no clear correlation (Figure 1(i) is duplicated for ease of comparison).

Figure 1(iii) reveals that twelve free lead content measurements are performed each day. Only these results are shown because the company places far more emphasis on monitoring and controlling free lead than apparent density. Although apparent density should be routinely measured, the difficulty of performing the procedure and the time involved in collecting the sample had resulted in the test becoming less used. At the start of the research only one density measurement was performed each week.

The daily variation in free lead content approximately covers the recommended specification range. For example, the average daily variation was from 19.3 to 27%. The week's variation was from 18.6 to 30.2%.

**Figure 1(iii) Variation in free lead content**

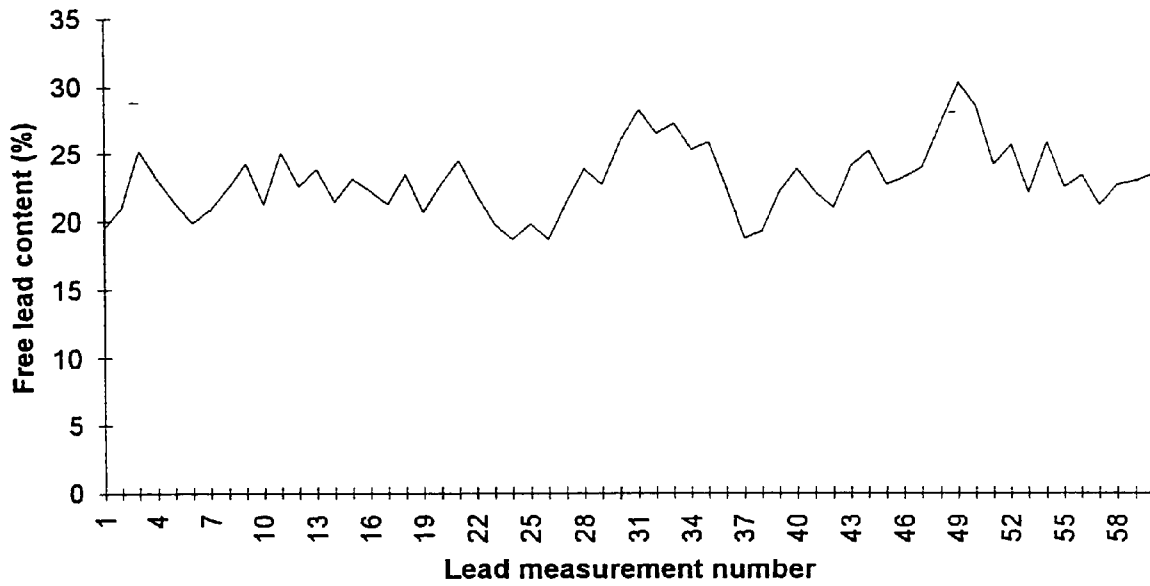


Fig. 1(iii)

**Figure 1(i) Variation in density measurements performed on freshly mixed positive pastes**

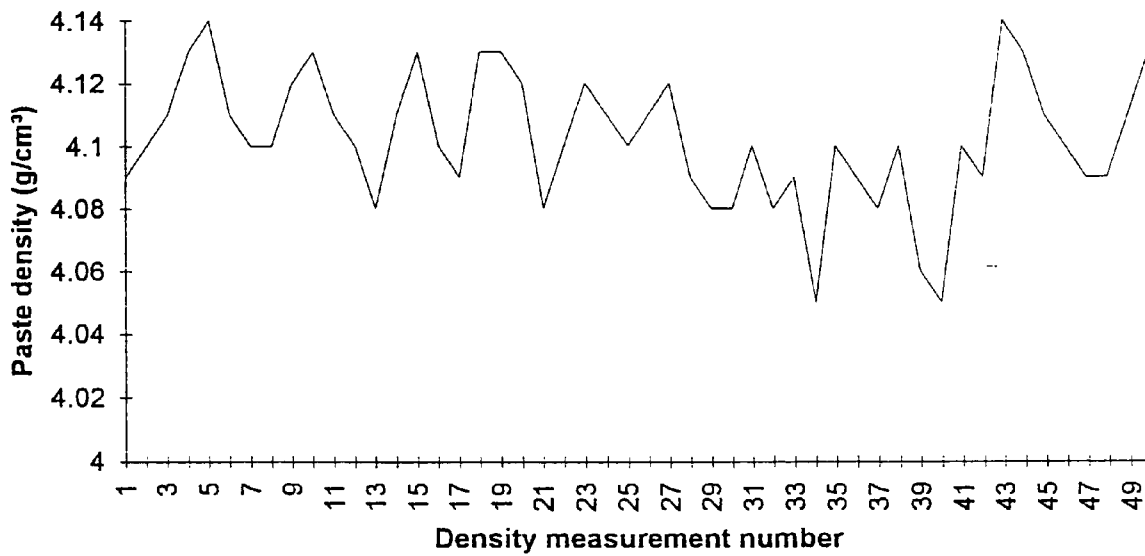


Fig. 1(i)



Comparison of the lead oxide free lead content (Figure 1(iii)) with paste density (Figure 1(i)) reveals that although both show large variations over the same period of time, no clear correlation can be seen. To accept the hypothesis that variations in paste density are due to lead oxide quality fluctuations, there should have been a good correlation between the two factors. However, lead oxide consistency is still believed to be the main variable which affects paste density since it is the major constituent of battery paste and is the only ingredient of battery paste which could be susceptible to large variations during production.

Therefore a reason for the far greater variation in lead oxide free lead content compared to paste density has to be determined.

#### 1.6 POSSIBLE REASONS FOR THE DISCREPANCY BETWEEN LEAD OXIDE FREE LEAD CONTENT AND PASTE DENSITY

Although paste composition (density) and lead oxide quality (free lead content) did not show a strong correlation, lead oxide quality was still considered to be the factor responsible for producing inconsistent paste density. Therefore before any further work could start on producing positive paste with a density of  $4.10 \text{ g/cm}^3$ , the reason for the

large variations in lead oxide free lead percentage had to be determined.

Two possible explanations which could be responsible for the observed lead oxide quality variations are:

(i) Problems associated with the quality tests

The first explanation considers the free lead property used to assess the quality of freshly produced lead oxide powder. The observed variations in Figure 1(iii) might not actually represent the true percentage free lead range. For example, the procedure used for measurement could be incapable of reproducible results, or the operators could be making experimental errors whilst performing the test.

The current test for measuring free lead requires performing a titration. The experimental procedure involved dissolving a weighed amount of lead oxide into a buffer solution which is titrated against E.D.T.A. The free lead is calculated from the weight of sample and the volume and concentration of E.D.T.A. used.

The initial stages of weighing and dissolving can be performed accurately. If errors occur in weighing only small variations in the measured content of free lead are obtained. For example, if samples are weighed with  $\pm 1 \times 10^{-3}$  g variation, this will affect the measurement of free lead by only  $\pm 0.08\%$ . The critical stage in determining the content of free lead is adding the E.D.T.A. solution from a burette. If errors are made reading the volume of E.D.T.A. added, considerable variations in the content of free lead will occur. For example, a  $\pm 0.1$  cm<sup>3</sup> variation in E.D.T.A. volume will result in a  $\pm 0.41\%$  variation in the content of free lead. The current free lead test was thoroughly investigated.

Also additional properties which could be used to routinely assess the quality of freshly produced lead oxide powder were investigated. If the investigation of the extant test for measuring free lead revealed that it was unsuitable for assessing lead oxide quality, a new test for measuring another property could be

introduced.

The properties which were considered capable of being used for assessing quality are introduced in Chapter 2 (The existing quality properties are also discussed).

(ii) Fluctuation of oxide mill process variables from their set-point conditions

If the free lead variation proves to be real and not an artefact of the measurements then the reason must be sought. The oxide mill process variables which are adjusted by the operator to manually control the free lead of freshly produced lead oxide powder could be fluctuating from their set-point values. This could have produced the observed percentage free lead variations in Figure 1(iii).

The process variables, airflow, ball mill charge level and ball mill temperature are adjusted by process operators to control the content of free lead. It is possible that one process variable could be varying

from its set point condition unnoticed. This could explain the large observed quality variations.

Although not strictly classed as process variables (operators cannot control them) the temperature and relative humidity of air drawn into the ball mill are dependent on the climatic conditions. Senior staff at the company believed that both the relative humidity and temperature of air influence the quality of freshly produced lead oxide powder. If true, then substantial variations in climatic conditions could produce fluctuations in lead oxide quality.

To determine whether the process variable fluctuations are the cause of lead oxide quality variations, a series of steady state sensitivity tests involving the process variables was carried out. Each variable was subjected to a large step up and step down test, whilst the other process variables were kept constant. It was hoped that each test would provide information on what effect each process variable has on free lead and apparent

density properties. This data could be used to develop a control system for automatically controlling lead oxide quality. Introducing an automated control system would remove the responsibility of the operators having to adjust process variables manually in order to control quality.

Once the ball mill process is brought under control, ranges of lead oxide quality can be experimented with to assess which ones are able to produce a paste density of 4.10 g/cm<sup>3</sup>. When this is achieved, the ball mill process can be set up to produce only that particular lead oxide quality.

#### 1.7 THE EFFECT OF LEAD OXIDE QUALITY ON PASTE COMPOSITION

Once the cause of the previously observed lead oxide quality variations was known and the ball mill process had been brought under control, trials were started to assess the effect of lead oxide quality on paste composition.

To determine whether a particular lead oxide quality produces a specific paste density, a series of paste mixing trials were performed, using samples of lead oxide containing various combinations of free lead

and apparent density. Once the combination of properties which produce a positive paste density of  $4.10 \text{ g/cm}^3$  was found, the oxide mill process was set up and controlled to produce only that specification of lead oxide.

The composition of each paste batch was assessed by measuring density. Each trial paste mix was performed in a specially commissioned experimental paste mixer. This was necessary because of the production demands imposed on the on-line paste mixer.

The composition of each trial batch of paste was also assessed by performing a stiffness test. Paste stiffness is defined as the flow resistance of paste to increasing force. It was hypothesised, based on operator experience, that variations in the stiffness of freshly mixed pastes could lead to problems during pasting. At pasting, a rotating twin bladed propeller contained in the pasting hopper forces paste into cast lead alloy grids. The blades are automatically controlled and the grid feeding rate is set, hence the only parameter capable of varying is paste stiffness. Paste is applied onto grids with consistent force, but if paste stiffness varies, problems could occur in the transfer of paste onto the grids. For example, the quantity (or thickness)

of paste added might vary, or the paste might not adhere.

Measuring both the density and stiffness of each trial batch of paste enabled the stiffness to be known at the ideal paste density. If paste stiffness appears to be too low at a density of  $4.10 \text{ g/cm}^3$ , a compromise can be reached (stiffness being too high has never been a problem). To be able to measure stiffness, a test had to be designed which would allow paste to be subjected to a range of forces to determine its shear force properties (see Chapter 5, Section 5.3).

As well as free lead and apparent density, the age of lead oxide is a factor which was believed to affect the composition of freshly mixed paste. Lead oxide produced at ball milling is conveyed to storage sites at the pasting area. It is either stored for days before use, or used within a couple of hours. The variation in the time of storage might have serious effects on the active material.

To determine what combination of the three lead oxide properties produce a density of  $4.10 \text{ g/cm}^3$ , required tests which are known as experimental optimisation tests. The trial involved performing a series of tests to determine an optimum combination of free



lead, apparent density and age. Three possible experimental design techniques could have been used.

## 1.8 EXPERIMENTAL OPTIMISATION TECHNIQUES<sup>16-18</sup>

The three approaches are:-

### (i) Classical Design

The classical approach is a one-dimensional test which involves varying one property whilst the other properties remain constant.

### (ii) Full Factorial Design

The three properties used to represent lead oxide quality can be divided into three levels (bottom, middle and top specification levels). If paste compositions are measured for all possible combinations of the chosen property levels, this is known as a complete factorial design. Three properties at three levels results in twenty-seven possible tests.

(iii) Fractional Factorial Design

The use of "orthogonal" arrays<sup>18</sup>, as for example by Dr. Genichi Taguchi, has introduced a very direct way to examine properties in an economical manner. The idea of using "orthogonal" arrays<sup>18</sup> for the design of experiments was studied independently in the United States and Japan during World War II.

Full factorial design would require twenty-seven experiments, the same test could be performed using fractional factorial design with only nine experiments, thus saving much time.

1.9 THE EXPERIMENTAL STAGES IN THE DEVELOPMENT OF  
CONSISTENT PASTE COMPOSITION

The steps undertaken during the Research Project are represented in Figure 1(iv).

Figure 1(iv) Schedule for developing consistent  
paste composition

DETERMINE THE REASON FOR THE LARGE VARIATIONS IN LEAD

OXIDE QUALITY MEASUREMENTS

- (i) Assess whether the reason was due to problems associated with the quality tests.
- (ii) Assess whether the reason was due to fluctuations of oxide mill process variables from their set point conditions.

EFFECT OF LEAD OXIDE QUALITY ON PASTE COMPOSITION

- (i) Determine the effect of lead oxide quality on paste composition, using experimental design principles.
- (ii) Develop an additional test to measure paste composition.
- (iii) Design an experimental paste mixer for mixing the experimental batches of paste.
- (iv) Use of statistical analysis techniques to determine the combination of lead oxide properties which produce a positive paste density of 4.10 g/cm<sup>3</sup>.

Figure 1(iv)

1.10 CHAPTER LAYOUT FOR BATTERY PASTE COMPOSITION PROJECT

Chapters Two, Three and Four deal with determining the reason for the large variations in lead oxide quality. Chapter Two introduces the various properties which can be measured in order to assess lead oxide consistency. These were investigated, so that if the free lead content test proved to be unreliable, another property could then be used to assess consistency.

Several properties were chosen as possible contenders

to replace the existing test. These were divided into:

(i) potential on-line test methods;

(ii) off-line test methods.

Both groups of properties were fully tested so that a decision could be taken on what type of test best suited the company's requirements. Chapter Three deals with the analysis of the potential on and off-line tests.

Chapter Four covers the work undertaken to determine whether the variation in lead oxide quality was due to uncontrolled variation of the oxide mill process variables.

Each process variable was subjected to a series of steady state sensitivity tests (whilst the other process variables are kept constant) during which time the response in both free lead and apparent density properties were measured. The results both for Chapter Three and Four are discussed at the end of Chapter Four and recommendations are given on how to produce lead oxide with consistent quality.

Chapter Five covers the optimisation tests which were

performed to determine the combination of lead oxide properties which produce a positive paste density of 4.10 g/cm<sup>3</sup>. An overall conclusion for the Project summarising the results, achievements and benefits to the company are given in Chapter Six. Chapter Seven is a section dedicated to recommendations for further research work in the sealed lead/acid battery field, based on the results obtained from this Project.

2.0        PROPERTIES OF LEAD OXIDE POWDER WHICH MAY BE USED TO  
ASSESS QUALITY

During the first twenty years of lead acid battery manufacture there was little literature available as to how batteries were produced. Each manufacturer followed their own "know-how", usually acquired through their own experimental efforts which they regarded as secret information. The secrecy, however, gradually declined due to the formation of Battery Associations. This resulted in an exchange of knowledge among members and stimulated the development of the technology in lead acid batteries.

Although the different manufacturers had different methods of producing lead oxide powder, each one realised that in order to produce batteries with consistent performance, they had to be able to produce lead oxide with a high degree of uniformity. The different methods of manufacturing lead oxide (see Chapter One, Section 1.2.1) produce varying quality lead oxide powders. For example, lead oxide with different quantities of alpha or beta lead oxide, different particle size distributions and shapes. However, irrespective of the manufacturing method, each manufacturer in the early days had four

laboratory procedures (properties) which served a useful purpose for controlling the oxide mill manufacturing process and to indicate the degree of uniformity of the final lead oxide produced.

The early laboratory procedures included a check for the presence of impurities (only very small amounts were permitted). Another determination which was used involved measuring the density of lead oxide powder. This determination is obtained from a simple apparatus which controls the fall of lead oxide from a sieve into a cup of known volume. It gives some indication of particle size. It is not an exact determination.

Another determination used at that time, is referred to as an acid absorption number for lead oxide. The acid absorption number of a lead oxide powder is an empirical determination of the relative particle size and surface area, based on the rate of reaction between lead oxide and sulphuric acid under arbitrarily chosen conditions of concentration, temperature, time and agitation.

The final property that was of interest in the production of lead oxide was the degree of oxidation or PbO (lead oxide) content. It is important that lead oxide be stable against any appreciable

continuing increase in lead oxide content for handling and storage purposes. The stability of lead oxide was considered to be in direct relation to the particle size. The finer the lead oxide, the more reactive it is and as such must have a higher PbO content for stability, whereas coarser lead oxide can be much lower in PbO content for the same degree of stability.

Although the various battery manufacturers had different processes for producing lead oxide, the mentioned tests were used to indicate the uniformity. Each of the tests could easily be performed in several minutes by a laboratory technician or process operator. However, the developments in the lead/acid battery industry over the last twenty years have introduced further determinations which serve as useful production control indicators. For example, the introduction of "intelligent" equipment which is capable of accurately measuring properties which were once very difficult and time consuming to determine.

There are a number of lead oxide properties which could be used as a routine test to assess its quality. Each property will be introduced in terms of the equipment required to perform the measurements and the lead oxide features being measured.



The various properties which could be monitored are given in Table 2(i).

Table 2(i)      Properties of lead oxide powder which are important

Lead oxide property to be measured	Lead oxide feature being measured	Recommended specification range
(i) Polymorphism	The preferred form of lead oxide has a tetragonal structure. The other form has an orthorhombic structure	The ball mill process is run below the transition temperature of 468°C to ensure production of the preferred tetragonal form.
(ii) Particle size	Particle size distributions determine the internal surface of active material, directly influencing polarisation during discharge.	> 50 micrometres 15% of particles should have this size. 5 to 50 micrometres 75% of particles should have this size. > 5 micrometres 10% of particles should have this size
(iii) Colour	Colour changes in lead oxide can be used to determine the content of PbO.	Lead oxide content range is approximately 70 to 80%.
(iv) Surface area and (v) Porosity	Variations in total pore volume, pore size distributions and porosity cause variations in paste consistency which influence polarisation during discharge.	Total pore volume range is 0.01 to 0.12 cm <sup>3</sup> /g. Pore size distribution is submicron to 30 micrometres. surface area range is 2 to 8 cm <sup>2</sup> /g.

Lead oxide property to be measured	Lead oxide feature being measured	Recommended specification range
(vi) Apparent density	An approximate production control device to check the uniformity of powder (a rough estimate of particle size)	Apparent density range is 0.95 to 1.25 g/cm <sup>3</sup> .
(vii) Acid absorption number	Provides information on paste making properties of lead oxide. Measurement of this property is a rough estimate of porosity.	Acid absorption range is 90 to 160 mg of sulphuric acid per gram of lead oxide.
(viii) Lead purity	Lead used to produce lead oxide should have high levels of purity.	The recommended maxima for each additional element present are: antimony 0.002%, arsenic 0.00005%, bismuth 0.05%, cadmium 0.003%, copper 0.003%, iron 0.02%, nickel 0.0001%, silver 0.003%, thallium 0.001%, zinc 0.002%, manganese 0.00003%.
(ix) Content of free lead	A certain amount of residual un-oxidised lead has to be present throughout each step of manufacturing active material.	The recommended specification range is 20 to 28%.
(x) Specular reflection to determine the content of free lead	Relating the content of free lead to the colour of freshly produced lead oxide powder	-

Table 2(i)

Table 2(i) reveals the lead oxide properties which are now capable of being measured. Each property has the potential to be regularly monitored in order to assess lead oxide quality. The ten properties are all very important to a battery's lifetime and performance. As a result, each property has a recommended specification range which must be adhered to.

To measure several of the properties requires sophisticated equipment. For example:

- (a) polymorphism requires an x-ray diffractometer;
- (b) particle size measurements can be performed using laser particle sizers, sedimentation processes and optical turbidimetry;
- (c) surface area requires a test known as the Brunauer, Emmet and Teller process (the BET process).<sup>22</sup>

Neither the polymorphism nor surface area properties were investigated due to a lack of facilities. The remaining properties were investigated and the results are analysed in Chapter Three.

## 2.1 INTRODUCTION OF THE PROPERTIES

### 2.1.1 Polymorphism<sup>3</sup>

The ball mill process of manufacturing lead oxide ensures that the predominant type produced is red tetragonal beta lead oxide and not the yellow orthorhombic form. To ensure this, the temperature of the process is kept below the transition temperature (468°C).

As the temperature set point of the ball mill process is considerably below the transition temperature, only the alpha form can be produced. Hence this property would never be measured on a regular basis to assess quality. Polymorphism would only be measured on an occasional basis to verify if the ball mill temperature has remained below the transition point.

### 2.1.2 Particle Size Variation<sup>15</sup>

The different methods for producing lead oxide have particle size ranges which vary considerably. (Table 2(ii)).

Table 2(ii)      Variation in particle size range for four different types of manufactured lead oxide

Commercial name of lead oxide	L-Dust	Velox Dust	Gox-Dust	Barton-Dust
Starting Material	Balls  (15 mm dia)	Balls or Bars (50 mm dia)	Bars	Molten Lead
Mill Type	Cylindrical Ball Mill	Conical Mill	Conical Mill with grind	Barton Mill
Particle range				
>50 micrometres	15%	30%	5%	5%
5 to 50 micrometres	75%	60%	45%	40%
< 5 micrometres	10%	10%	50%	55%

Table 2(ii)

A number of methods have been tried to measure particle size. Visual examination requires the use of an optical microscope and graticule. Sedimentation processes determine particle size by measuring the particles' velocities when allowed to fall under the force of gravity in an air or water medium.

However, the method of choice has become laser diffraction. Laser particle sizers consist of laser transmitter and receiver detector units into which the samples under analysis are passed. Laser

diffraction sizing is based on the principle that small particles diffract light to large angles, whereas large particles diffract it to small angles. By measuring the scattered light intensity it is possible to determine particle size. A computer displays the analysed data as particle size distributions. It is considered fast, reliable and simple to use, not only for research but also routinely for quality and process monitoring. This method was the one chosen to measure the particle size range of the company's ball mill lead oxide powder.

The key to every valid test is a valid sample. It is therefore essential that the slurry that passes through the sample cell is a true representation of the material being tested. The instrument's flow system provides an even stream of sample. There are no corners or pockets where heavier particles could be trapped. A high volume pump pushes particles through the sample cell four times a minute and keeps heavier particles in suspension. If desired an ultrasonic mixer is activated to maximise dispersion.

The sizer used was one which allowed the sample to be dispersed in a reservoir of ethanol prior to being passed into the sample cells. To aid dispersion of the particles, ultrasonics were applied to each

slurry for two minutes.

#### 2.1.3 Colour<sup>7</sup>

Lead oxide can vary from greenish black through yellow-green to yellow-red, depending on the subdivision and content of free lead. The colour cannot be used as proof of the presence of red or yellow lead oxide. However, a measurement of colour could perhaps be used to determine the content of free lead.

#### 2.1.4 Surface Area<sup>22</sup>

A method developed by Brunauer, Emmet and Teller (the BET process) can be used to measure surface area. The principle of the method involves measuring the volume of gas physically adsorbed as a monolayer on the surface. Knowing the area that one adsorbate molecule occupies, the total surface area can be calculated.

A number of gases may be used as the adsorbate for determining surface area. The most commonly used is nitrogen. In order to be able to test samples, they first have to be degassed. This is achieved by heating them for several hours under vacuum at a temperature of 100 to 400°C.

#### 2.1.5 Porosity<sup>15</sup>

The measurement of pore size and pore distribution requires the use of a mercury porosimeter. Mercury is used as it does not wet the material under test.

To analyse the pore distributions and sizes requires that samples be held in small pressure vessels filled with mercury and the volume changes noted at increasing and decreasing pressure steps.

#### 2.1.6 Apparent density<sup>7</sup>

The method used to measure apparent density involves sifting a sample of lead oxide through a mesh (mesh aperture is 0.784 mm and mesh diameter is 0.274 mm) and collecting the sample in a holder of known volume. The next step is to weigh the full holder. The value which is expressed in grams per cubic centimetre has become a well established test in industry and if performed carefully can serve as a useful means for controlling plant manufacturing processes to indicate the degree of uniformity of the lead oxide product.

#### 2.1.7 Acid absorption number<sup>7</sup>

The procedure for determining the acid absorption



number for a given lead oxide powder involves reacting 1.4 specific gravity sulphuric acid with an accurately weighed sample of lead oxide powder. The reaction is agitated at room temperature (25°C) for a controlled length of time.

The final results of acid absorption tests are expressed in terms of gram weight of sulphuric acid absorbed by one gram of lead oxide powder. Generally a high acid absorption number indicates a fine particle size and this is expressed by a high numerical figure. A low acid absorption number indicates coarse particle sizes.

#### 2.1.8 Lead purity<sup>15</sup>

Lead with high levels of element purity is used in the manufacture of lead oxide. All measurements are performed on an atomic absorption spectrometer. Table 2(iii) reveals the typical quantities of elements which are present.

Table 2(iii) Acceptable purity levels for lead used in the production of lead oxide

Element	Percentage not to exceed (% wt)	Element	Percentage not to exceed (% wt)
Antimony	0.002	Nickel	0.0001
Arsenic	0.00005	Silver	0.003
Bismuth	0.05	Thallium	0.001
Cadmium	0.003	Zinc	0.002
Copper	0.003	Manganese	0.00003
Iron	0.02		

Table 2(iii)

#### 2.1.9 The content of free lead<sup>7,9</sup>

Free lead is considered an important process variable in the control of lead oxide manufacture. The recommended specification ranges for the different methods of manufacture vary enormously. In ball milling the free lead content range is from 20 to 28%.

During manufacture, control of free lead involves the correlation of the following variables: degree of lead agitation; size of operating load; amount of air supply and operating temperature. Free lead is measured by performing a titration. It involves dissolving a weighed sample of lead oxide into a buffer. The mixture is titrated against E.D.T.A. The volume and concentration of titre used, divided by the weight of lead oxide used, provides the

content of free lead.

Another standard method which could be used, involves using a 1:3 ratio by volume of glacial acetic acid and deionized water solution. This readily dissolves lead oxide but only very slowly attacks pure lead. The lead which remains, now in the spongy form, is dried and weighed. By simple calculation, the content of free lead in the original weighed sample is determined.

#### 2.1.10 Specular or fresnel reflection to determine free lead

The colour of ball mill lead oxide is supposed to vary depending on the subdivision and quantity of free lead present. The colour changes which are thought to occur could be very difficult to see. Therefore it is important to use equipment which has the potential to accurately measure colour changes. A technique which can be used is specular reflectance. The unit chosen to perform the reflectance work is a fixed angle reflectance unit, with the angle of incidence fixed at approximately 16 degrees.

A number of the properties were analysed to determine the ones with the potential for being routinely measured to assess lead oxide quality. The

experimental procedures used for measuring the properties can either be performed on-line, where lead oxide samples can be analysed without being physically removed from the oxide mill process, or, off-line, where samples of lead oxide have to be physically removed from the oxide mill process and analysed some time later. The details and results of the experimental procedures which fall into both categories are given in Chapter Three.

## CHAPTER THREE

### 3.0      INVESTIGATION OF THE LEAD OXIDE PROPERTIES TO DETERMINE WHICH ONES COULD BE USED TO ROUTINELY ASSESS THE QUALITY OF FRESHLY PRODUCED LEAD OXIDE POWDER

Two possible explanations for quality variation were tested. The first considered that quality variations could be due to errors associated with the experimental procedure used for measuring free lead. This could result from the test procedure producing inaccurate results. The second explanation, considered that the consistency variations were real and were due to the ball mill process variables varying from their set point conditions (This latter idea is discussed in Chapter Four).

As a precautionary measure, further experimental procedures for measuring other lead oxide properties were investigated to assess which properties could be measured on a regular routine basis for assessing the quality of freshly produced lead oxide powder. If the investigation of the experimental procedure for determining free lead proved that it was unreliable, another property could be introduced as the quality control test.

The experimental procedures for measuring the lead oxide properties, particle size, colour, free lead, apparent density and acid absorption were investigated.

The first experimental procedure investigated was the technique of measuring particle size using lasers.

### 3.1      PARTICLE SIZE

Lead oxide particle size is a property which is capable of being used as a production control test to assess the quality of freshly produced ball mill lead oxide powder. Particle size is an important property to control because of its effect on the internal surface of active material. If variations in particle size were occurring during production, batteries could suffer polarisation defects during use which would result in shorter battery life expectancy.

In Chapter Two, procedures such as sedimentation and optical turbidimetry were introduced as possible tests for measuring particle size. However, these procedures could not be considered for use as a routine production control test. These procedures, although being capable of accurately measuring particle size, are far too involved and time-

consuming to be performed every two hours by the oxide mill operators.

The laser technique for measuring particle size was considered the most promising method for routine use as a production test. The manufacturers of laser particle equipment claim that particle size results achieved via the laser procedure are as accurate as particle size results achieved using the time-consuming and difficult technique of using a scanning electron microscope (SEM) with a calibrated graticule.

The experimental procedure for laser particle size determinations has been discussed in Chapter Two. However, the general experimental procedure involved thoroughly mixing the powdered lead oxide sample by spatula. A portion was placed into a small glass beaker (50 cm<sup>3</sup>). Approximately 10 cm<sup>3</sup> of dispersant (ethanol) was added to the powder and a slurry was made after thorough mixing. If on viewing the slurry, agglomerates appear to be present (usually found at the bottom of the beaker), ultrasound was applied to help break down the larger clumps into primary particles.

If samples are to be analysed correctly, it is necessary to have a good dispersion. The time for an

analysis takes approximately one minute. Menu driven software interfaced with a computer collects the data and presents it graphically.

If however, it was decided that full dispersion had been achieved, or if it was difficult to ascertain whether or not this was the case, the sample was analysed without the application of ultrasonics. The sample was measured by adding a few drops of the slurry to the neat dispersant in the measurement cell. Several successive measurements had to be made over a period of time to ensure that the particle size remained stable. If this was the case, no further work was necessary.

However, if a decrease in particle size was seen, indicating that the particles were still dispersing, the whole procedure had to be repeated. But this time the beaker containing the slurry was placed into an ultrasonic bath for between two and ten minutes, after which the slurry was added to the measurement cell for analysis. Again several successive measurements had to be made over a period of time to ensure that the particle size remained stable. Further ultrasound was applied as necessary, until stability was achieved.

Particle size determinations were performed over a



period of one month. Over the trial period, a Malvern Instruments laser particle sizer (Mastersizer X) was used. All lead oxide samples which were collected over the one month were analysed at Malvern Instruments Applications Laboratory.

Three particle size determinations were performed on each individual sample sent to Malvern Instruments. After discussions with Malvern Instruments laboratory technicians, three size determinations on individual samples was considered sufficient to determine if a laser particle sizer was capable of consistently obtaining reproducible results. Provided representative lead oxide powder dispersions are prepared, the laboratory technicians at Malvern Instruments claim that the Mastersizer X is capable of measuring particle size distributions of individual samples with a repeatability of  $\pm 1\%$ . Thirty one particle size distributions were carried out at Malvern Instruments technical laboratory. [Six particle size distributions which were obtained are shown later. The percentage particle size distributions of the remaining samples are included in the Appendix (Table A(i))].

The range between the three consecutive measurements for each size category (i.e.  $< 5 \mu\text{m}$ ,  $5 \text{ to } 50 \mu\text{m}$  and  $> 50 \mu\text{m}$ ) will be assessed and depending on the

reproducibility between the results the suitability of the laser method as a possible production control test for assessing lead oxide quality will be considered. If the three particle size determinations for individual samples correlate (that is, the percentage volume of particles must be within  $\pm 1\%$  of each other for the three different particle size ranges measured), a further particle size determination using the accurate technique of graticule and SEM would be performed. This would confirm whether the laser technique produced size determinations which were as accurate as the graticule method. If the results for both methods agreed, the laser particle sizer could be considered as a possible production control test for routinely assessing the quality of freshly produced lead oxide powder.

#### 3.1.1 RESULTS OF LEAD OXIDE SAMPLES ANALYSED USING A LASER PARTICLE SIZER

Samples of freshly produced ball mill lead oxide should have the typical size distribution shown in Table 3(i).

Table 3(i) Typical particle size distribution for fresh ball mill lead oxide powder

Particle size range	Volume (%)
> 50 $\mu\text{m}$	15
5 to 50 $\mu\text{m}$	75
< 5 $\mu\text{m}$	10

Table 3(i)

The general particle size results in Table 3(i) were obtained using the SEM and graticule procedure (Courtesy of Yuasa Corporation central research laboratories in Tokyo). The volume of particles in each category is considered to be the recommended specification range for freshly produced ball mill lead oxide. The particle size determinations performed by the laser sizer on lead oxide samples taken over the one month trial period are shown in Table 3(ii). The results have been presented as the percentage volume of particles at the size ranges of <5  $\mu\text{m}$ , 5 to 50  $\mu\text{m}$  and >50  $\mu\text{m}$ . For each individual sample, three size determinations have been performed and the particle size range has also been shown.

Analysis of the three size determinations for each individual sample, revealed considerable range in the percentage volume of particles in each size category. For each individual sample the percentage volume of particles at each particle size range revealed variations which were far greater than the

repeatability accuracy of  $\pm 1\%$  claimed by Malvern Instruments. The variation displayed in Table 3(ii) could not be tolerated. The results clearly revealed that the laser sizer could not be considered as a procedure for consistently measuring lead oxide particle size.

Table 3(ii) Results of particle size determinations using a laser sizer

Sample number	Percentage of particles <5 micro-metres	Range (%)	Percentage of particles 5 to 50 micro-metres	Range (%)	Percentage of particles >50 micro-metres	Range (%)
1	8 55 25	8-55	72 33 10	10- 72	20 12 65	12-65
2	9 56 30	9-56	60 28 4	4-60	31 16 66	16-66
3	8 79 25	8-79	30 10 50	10- 50	62 11 25	11-62
4	39 71 5	5-71	55 3 35	3-55	6 26 60	6-60
5	10 62 20	10- 62	74 2 20	2-74	16 36 60	16-60
6	55 10 35	10- 55	5 72 40	5-72	40 18 25	18-40

Table 3(ii)

Malvern instruments have considerable expertise in determining the particle size distribution of powders. However, they experienced considerable

problems analysing the samples of lead oxide powder. The feedback from Malvern instruments laboratory technicians revealed they were unable to produce reliably fully dispersed slurries. The lead oxide samples appeared to "fall out" of solution and agglomerate. The laboratory technicians believed that it was the agglomeration of the lead oxide particles which affected the reliability of the procedure.

On completion of the trial, Malvern Instruments explained that no more could be done to aid the dispersion of the lead oxide samples prior to injection into the sample cell ( Section 3.1). They claimed that all the standard procedures had been used but none had proved successful. As a result, Malvern Instruments concluded that using the laser method for measuring lead oxide particle size would not be advisable. Their inability to overcome the dispersion problems coupled with the poor "flow" properties (i.e. unable to be analysed dry) of lead oxide resulted in Malvern Instruments admitting that the results from the laser particle sizer were far too inconsistent to be used as a production quality control test.

Because of the large variations in the measured particle size ranges, no further size determinations

using the graticule and SEM technique were thought necessary. It was disappointing that the laser sizer was found to be inconsistent as it had the potential to be developed into an automated on-line test for assessing the quality of freshly produced lead oxide powder.

The conclusion from the laser sizer trials revealed that the particle size of freshly produced lead oxide could not be used as a routine production test for assessing the quality of freshly produced lead oxide powder. Although a recommended specification range for particle size exists, the failure of the laser technique means that no experimental procedures are capable of accurately determining the size range in the short time period required for the routine analysis of lead oxide samples during production. Therefore the determination of particle size ranges was not further investigated as a possible replacement to measuring the free lead property.

### 3.2 SPECULAR REFLECTANCE

The colour of freshly produced ball mill lead oxide is prone to variations from greenish-black to yellow-green. The measurement of lead oxide colour was considered as a potential production test for assessing lead oxide quality. The colour variations were thought to be dependent on the quantity of free

lead. If the free lead content of freshly produced lead oxide powder influenced colour, it might be possible to determine the quantity of free lead by measuring the colour of a sample. If such a correlation were discovered, a new procedure for measuring free lead could be introduced as a new production control quality test.

The technique used for measuring the colour of powders is specular reflectance (see Chapter Two, Section 2.1.10). A spectrophotometer housing a specular reflection unit measures the percentage of ultra violet and visible light which a powder absorbs over a wavelength range of 300 to 800 nanometres (nm). If a correlation between lead oxide colour and free lead were proven, a recommended specification range could be introduced in terms of an absorbance value at a particular wavelength for a corresponding content of free lead.

The reflectance work was performed on a Cecil Instruments spectrophotometer (model u.v. 5000) at the University of Glamorgan. The spectrophotometer was software driven. It was controlled by a remote P.C. through a built-in RS232 interface. The P.C. controlled all activities, including cell programming, wavelength programming and scanning. The instrument had a double beam optical system which

ensured much greater stability than single beam optical systems, both in terms of drift and stability of baseline. The lamp used was a tungsten halide type.

The initial step in performing a specular reflection analysis was to set the wavelength to the desired range. For lead oxide the scan range was from 300 to 800 nm. The second step was to enter a base line for the wavelength range being used. This was performed by filling both sample holders with magnesium oxide (MgO) powder and placing in the sample and reference beams of the spectrophotometer. On pressing the scan button, a new base line was created. Throughout the duration of the analysis, the sample holder filled with MgO remained in the reference beam. Samples of lead oxide were carefully placed in the sample holder and inserted into the sample beam. The scan time was set to five minutes. Menu driven software plotted a profile of absorbance against wavelength.

### 3.2.1 TESTS TO ASSESS THE REPRODUCIBILITY OF THE SPECULAR REFLECTANCE EXPERIMENTAL PROCEDURE

To determine if the colour property could be used as the basis for a production test for routinely assessing the quality of freshly produced lead oxide powder, the specular reflectance procedure had to

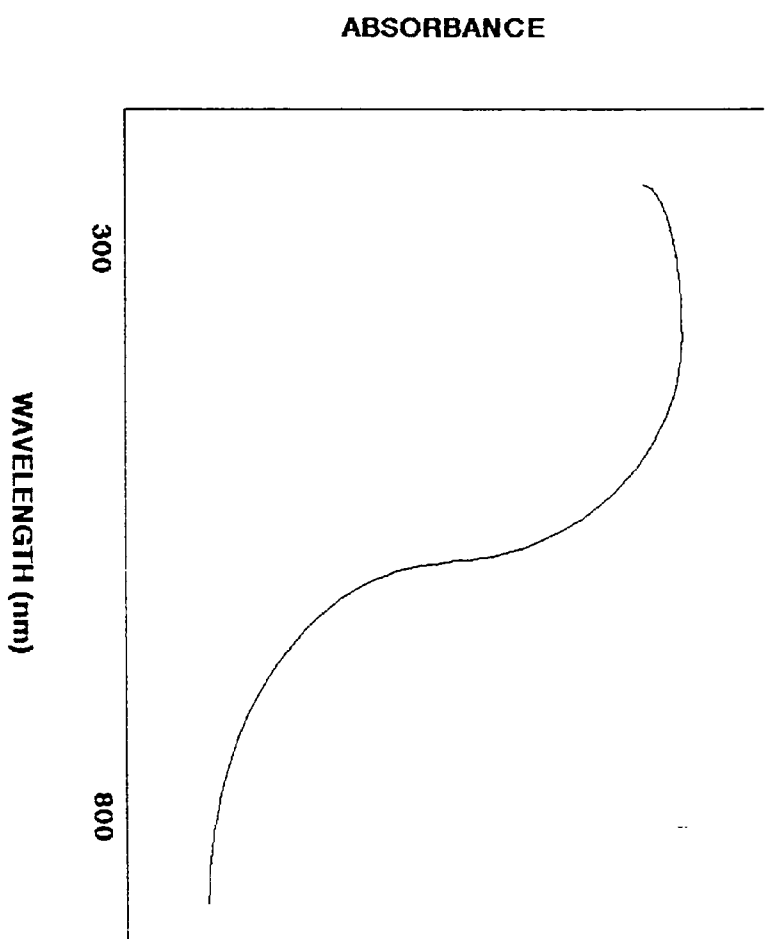


demonstrate that it was capable of reproducible results. This was tested by analysing ten samples. Five absorbance profiles were performed on each individual sample (for each absorbance run, samples were packed and emptied from the sample cell). The quantity of free lead in the sample was determined before the commencement of the specular reflection tests using the existing titration procedure.

The absorbance profiles for the lead oxide sample over the wavelength range of 300 to 800 nm produced characteristic curves (Figure 3(i)).

The absorbance difference between 300 and 800 nm was used to compare each profile. At each of these wavelength points the respective maximum and minimum absorbance values for each profile occurred. Table 3(iii) summarises the results. Other parameters of the absorbance profile were investigated, but the absorbance difference between 300 and 800 nm appeared the best characteristic to use for comparison purposes.

**FIGURE 3(i)**      Characteristic absorbance profile for lead oxide powder



**Fig. 3(i)**

Table 3(iii) Evidence of reproducibility using the specular reflectance procedure

Sample number	Free lead content (%)	Absorbance difference between 300 and 800 nm	Mean absorbance difference	Standard deviation
- 1	22.3 " " " "	0.820 0.821 0.822 0.820 0.820	0.821	8.94x10 <sup>-4</sup>
2	23.1 " " " "	0.791 0.790 0.792 0.792 0.791	0.791	8.36x10 <sup>-4</sup>
3	21.8 " " " "	0.873 0.872 0.872 0.871 0.872	0.872	7.07x10 <sup>-4</sup>
4	25.6 " " " "	0.821 0.820 0.822 0.821 0.820	0.821	8.36x10 <sup>-4</sup>
5	26.2 " " " "	0.915 0.915 0.916 0.916 0.917	0.916	8.36x10 <sup>-4</sup>
6	20.5 " " " "	1.091 1.090 1.091 1.091 1.092	1.091	7.07x10 <sup>-4</sup>
7	23.4 " " " "	0.845 0.845 0.844 0.844 0.844	0.844	5.47x10 <sup>-4</sup>
8	24.6 " " " "	1.010 1.011 1.011 1.012 1.010	1.011	8.36x10 <sup>-4</sup>
9	27.3 " " " "	0.810 0.811 0.812 0.811 0.810	0.811	8.36x10 <sup>-4</sup>
10	23.6 " " " "	0.952 0.953 0.953 0.953 0.954	0.953	7.07x10 <sup>-4</sup>

Comparison of the absorbance differences for each curve revealed that no variations had occurred between profiles for individual samples. The low standard deviations confirmed the reproducibility of the experimental procedure.

### 3.2.2 CORRELATION OF THE SPECULAR REFLECTANCE TEST RESULTS TO FREE LEAD CONTENT

Having established the reproducibility of the specular reflectance procedure, the next stage was to collect lead oxide samples over a period of one month, calculate the free lead using the titration procedure and then perform an absorbance profile on each sample. All analysis and sample preparation was performed by myself at the University of Glamorgan. Five absorbance profiles for each sample were performed. Table 3(iv) summarises the results.

Table 3(iv) Absorbance profiles and free lead values of lead oxide samples collected over one month

Sample number	Free lead content (%)	Absorbance difference between 300 and 800 nm	Mean absorbance difference	Standard deviation
1	22.5	0.915 0.915 0.916 0.916 0.915	0.915	$5.47 \times 10^{-4}$
2	26.8	0.996 0.998 0.997 0.997 0.996	0.997	$8.36 \times 10^{-4}$
3	25.1	0.996 0.997 0.997 0.996 0.996	0.996	$5.47 \times 10^{-4}$
4	20.2	1.090 1.090 1.091 1.092 1.091	1.091	$8.36 \times 10^{-4}$
5	21.5	0.961 0.962 0.961 0.962 0.962	0.962	$5.47 \times 10^{-4}$
6	26.9	0.986 0.988 0.987 0.987 0.986	0.987	$8.36 \times 10^{-4}$
7	22.4	1.042 1.043 1.043 1.042 1.041	1.042	$8.36 \times 10^{-4}$
8	23.2	0.950 0.951 0.952 0.951 0.952	0.951	$8.36 \times 10^{-4}$
9	23.8	0.972 0.970 0.971 0.972 0.970	0.971	$1 \times 10^{-4}$

Sample Number	Free lead content (%)	Absorbance difference between 300 and 800 nm	Mean absorbance difference	Standard deviation
10	22.5	0.937 0.938 0.938 0.937 0.939	0.938	$8.36 \times 10^{-4}$
11	21.3	1.009 1.007 1.008 1.008 1.009	1.008	$8.36 \times 10^{-4}$
12	24.6	1.042 1.040 1.041 1.041 1.041	1.041	$7.07 \times 10^{-4}$
13	21.2	0.996 0.997 0.997 0.996 0.997	0.997	$5.47 \times 10^{-4}$
14	21.5	1.031 1.032 1.033 1.032 1.031	1.032	$8.36 \times 10^{-4}$
15	21.9	0.880 0.881 0.882 0.881 0.880	0.881	$8.36 \times 10^{-4}$
16	22	0.891 0.890 0.892 0.891 0.891	0.891	$7.07 \times 10^{-4}$
17	20.2	0.996 0.998 0.997 0.997 0.998	0.997	$8.36 \times 10^{-4}$
18	25.5	0.996 0.998 0.997 0.997 0.996	0.997	$8.36 \times 10^{-4}$
19	25.2	0.845 0.844 0.846 0.845 0.845	0.845	$7.07 \times 10^{-4}$

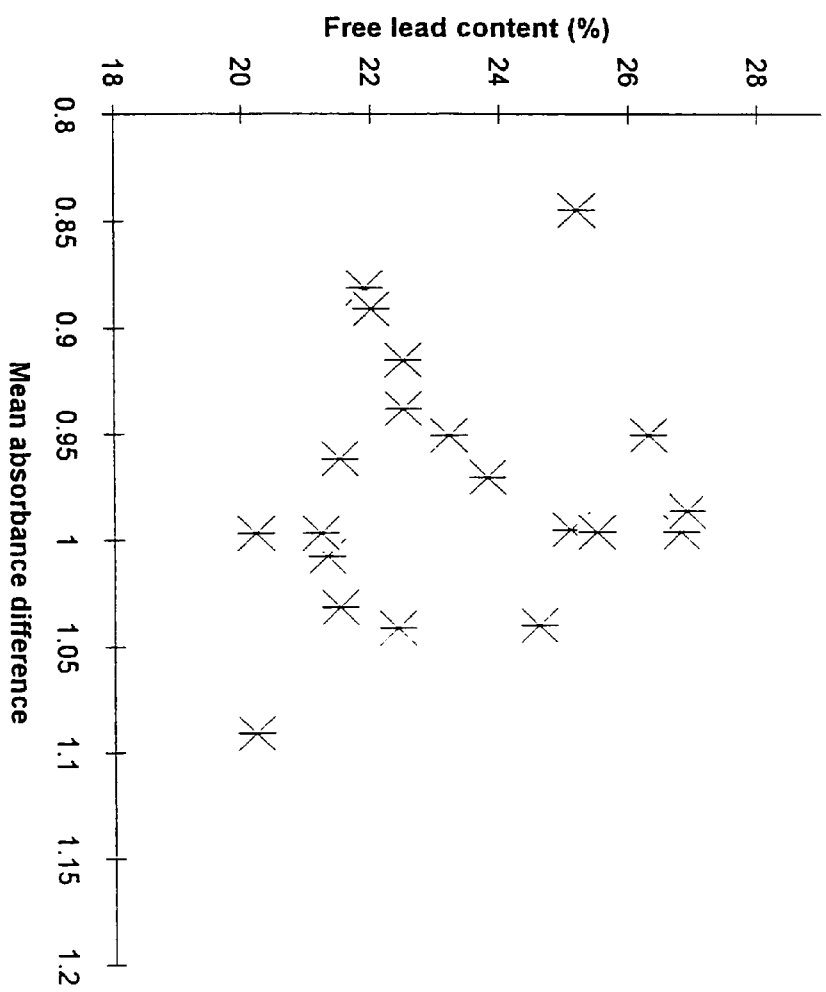
20	26.3	0.950 0.951 0.951 0.952 0.950	0.951	$8.36 \times 10^{-4}$
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Table 3(iv)

The mean absorbance difference and free lead values for each sample were plotted against one another (Figure 3(ii)). Analysis of the scatter plot revealed that the mean absorbance difference and free lead data revealed no correlation. As a result, no further colour measurements using the specular reflectance procedure were performed. Therefore the technique of using specular reflectance to assess lead oxide quality could no longer be considered as a possible quality test for production control. This was disappointing because the specular reflectance procedure had the potential to be modified into an automated on-line test.

If a relationship between absorbance and free lead values had been discovered the P.C. controlled specular reflectance procedure could have been further developed to enable a fully automated sample preparation and measurement procedure to be introduced on line with each ball mill.

**Figure 3(ii) Scatter plot of mean absorbance differences against free lead contents of lead oxide samples collected over one month**



**Fig. 3(ii)**



### 3.3

#### FREE LEAD

Directly measured free lead in an off line test is the current property used to assess the quality of freshly produced ball mill lead oxide. It is an important property to monitor and control because of its role during pasting and the subsequent stages of active material production (Chapter One, Section 1.2). Free lead provides an energy source via its own oxidation, which allows the growth of certain crystalline compounds which are capable of forming rigid interlacing fibrous materials which are required to ensure that battery electrodes function efficiently during charge/discharge reactions. The recommended specification range for free lead is 20 to 28%. If lead oxide can be produced with free lead within the specification range, it is assumed to be of acceptable quality for producing battery paste.

#### 3.3.1

##### THE EXPERIMENTAL PROCEDURE USED FOR MEASURING FREE LEAD

There are two procedures which can be used for measuring free lead:

##### (i) The acetic acid method<sup>7</sup>

This is the most popular procedure for

measuring free lead in a lead oxide sample. The procedure involves boiling a weighed sample of lead oxide in a 1:3 ratio (by volume) of glacial acetic acid and deionised water. The coagulated lead residue is washed with water, the excess liquid from the lead residue is removed and the residue is dried in an oven at 130°C for fifteen minutes. The dried sample is cooled in a desiccator and weighed on an analytical balance.

The calculation used to determine the free lead is given in Equation 3(i).

Equation 3(i)

$$\text{Free lead \%} = \frac{\text{Wt. of residue}}{\text{Wt. of lead oxide sample}} \times 100$$

(ii) The titration method

This is the standard procedure used at the company. The procedure involves adding a weighed sample of lead oxide powder to a beaker of deionised water, acetic acid, ammonia and xylenol orange. The resulting mixture is stirred and heated for five minutes, whereupon it is titrated against standard ethylene diamine tetraacetic acid (E.D.T.A) solution.

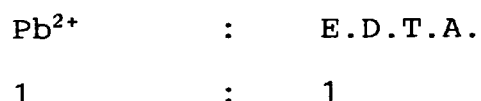
The acidity is sufficient to dissolve lead oxide but not lead. This releases lead(II) ions into solution

which form a complex with xylenol orange. This results in a colour change from orange to purple. The lead particles agglomerate to form a stone which does not interfere with the titration.

E.D.T.A. complexes with lead during the titration. At the end point, xylenol orange is displaced by E.D.T.A. to form a characteristic colour change from purple to yellow. The equation used to calculate free lead was derived as follows.

In the E.D.T.A. titration, lead(II) ions react 1:1 with E.D.T.A. The steps in the derivation are represented in Equations 3(ii) - 3(v).

Equation 3(ii)



Equation 3(iii)

$$\text{Number of moles EDTA (M}_{\text{EDTA}}) = \frac{C_E \cdot V_E}{1000} = \text{Number of moles lead (M}_{\text{lead}})$$

where:  $C_E$  - concentration of E.D.T.A. in mol/dm<sup>3</sup>

$V_E$  - volume of E.D.T.A. in cm<sup>3</sup>

$M_{\text{lead}}$  = Number of moles Pb<sup>2+</sup> (PbO)

Equation 3(iv)

$$\text{Mass of lead oxide per sample} = M_{\text{lead}} \times M_{\text{r lead oxide}}$$

Where:  $M_{r_{\text{lead oxide}}}$  = Relative Molar Mass of lead oxide

$$M_{r_{\text{lead oxide}}} = 224$$

The relationship for the number of moles of lead(II) ions in terms of volume and concentration of E.D.T.A. is substituted into Equation 3(iv). Rearrangement of the variables gives the equation which is used to calculate the content of free lead (Equation 3(v)).

#### Equation 3(v)

$$\text{Free lead content} = 100 - \left( \frac{\text{mass oxide}}{\text{total mass}} \times 100 \right)$$

### 3.3.2 VARIATION IN FREE LEAD VALUES MEASURED USING THE TITRATION PROCEDURE

Analysis of previously observed free lead results has revealed considerable variations in quality (see Chapter One, Figure 1(iii)). Using the titration procedures, twelve free lead determinations were performed each day. The daily variation in results exceeded the recommended specification range. The typical daily variation was from 19 to 27%, whereas the weekly variation was from 18 to 30%.

Two possible explanations for the free lead variations shown in Chapter One (Figure 1(iii)) could be experimental error in performing the titration procedure or variation in the ball mill process

variables. Investigation of both hypotheses would confirm whether the variations in free lead were real (i.e. the observed variations actually occurred and were the result of the ball mill process variables fluctuating) or spurious (i.e. the ball mill process was stable, but experimental errors in performing the titration procedure affected the accuracy of the free lead calculation).

Possible errors associated with the titration procedure were the first point tested (Possible fluctuations in the ball mill process variables were investigated separately).

To assess whether the experimental errors were a cause of previously observed variations in free lead, samples of lead oxide were collected over a period of one month and the free leads for individual samples were determined by myself, the oxide mill operators and trained laboratory technicians. The results from both groups were compared. Three titrations were performed on each sample.

Table 3(v) reveals the results which were obtained. The mean, range and standard deviation of each sample was calculated.

The oxide mill operators analysed all the samples whereas myself and the laboratory technicians

analysed half each. The first ten samples were analysed by myself whereas the remainder were done by the laboratory technicians

Analysis of the free lead determinations carried out on individual samples by the oxide mill operators revealed considerable variation. The range varied from 1.5 to 2.8% and the standard deviation varied from 0.9 to 1.5. Comparison with the free lead determinations carried out on the same samples by myself and the laboratory technicians revealed that the range in free lead values for individual samples was 0.6 to 0.7% and the standard deviation was 0.3 to 0.4. The results of both myself and the laboratory technicians clearly demonstrated that if the procedure was performed accurately consistent reproducible free lead results could be achieved with a range of  $\pm 0.3\%$  and a standard deviation of 0.3 to 0.4%.

Table 3 (v) Analysis of free lead data measured by myself, the oxide mill operators and laboratory technicians

Sample number	Free lead content calculated by the oxide mill operators (%)	Range (%)	Mean free lead content (%)	Standard deviation	Free lead content calculated by both myself and laboratory technicians (%)	Range (%)	Mean free lead content (%)	Standard deviation
1	24 23.8 22.4	1.6	23.4	0.9	22.6 23 22.4	0.6	22.7	0.3
2	23.1 25.5 25.9	2.8	24.8	1.51	24.2 24.6 24.6	0.6	24.5	0.3
3	21.9 23.6 22.3	1.7	22.6	0.9	21.4 21.9 22.1	0.7	21.3	0.4
4	23.5 22.1 24.6	1.5	23.4	1.3	22.9 23.5 23.3	0.6	23.2	0.3
5	26.6 24.3 25.1	2.3	25.3	1.2	24.3 24.7 25	0.7	24.7	0.4
6	22.5 23.8 24.4	1.9	23.6	1	23.2 23.8 23.5	0.6	23.5	0.3
7	25.2 26.9 25.9	1.7	26	0.9	25 24.8 25.4	0.6	25.1	0.3
8	23.4 22.8 24.7	1.9	23.6	1	22.6 21.9 22	0.7	22.2	0.4
9	23.2 25.3 24.1	2.1	24.2	1.1	22 22.7 22.3	0.7	22.3	0.4
10	24.4 26 25.1	1.6	25.2	0.8	23.8 23.4 23.9	0.6	23.7	0.3
11	24.1 25 23.2	1.8	24.1	0.9	22.9 22.3 22.7	0.6	22.6	0.3
12	24.4 22.9 23.9	1.5	23.7	0.8	22 22.6 22.4	0.6	22.3	0.3
13	24.1 24.9 25.6	1.5	24.9	0.8	23.5 23.9 24.2	0.7	23.9	0.4
14	26.3 25.1 24.3	2	25.2	1	24 23.4 23.9	0.6	23.8	0.3
15	27.2 29 28.2	1.8	28.1	0.9	26.2 26.8 26.4	0.6	26.5	0.3
16	22.8 24 24.9	2.1	23.9	1.1	22.5 23.2 22.8	0.7	22.8	0.4
17	24.2 25.4 26	1.8	25.2	0.9	22.8 23.4 23.1	0.6	23.1	0.3
18	22.1 21.2 23.2	2	22.2	1	21.1 20.8 21.4	0.6	21.1	0.3
19	24.2 25.3 26.1	1.9	25.2	1	23.5 24.2 23.7	0.7	23.7	0.4
20	25.9 24.2 24.4	1.5	24.8	0.9	22.9 22.2 22.6	0.7	22.6	0.4

Table 3(iv)

The operators' results revealed that they did not have the required analytical skills needed to perform the titration procedure accurately. My results clearly demonstrated that if the procedure was performed accurately, consistent reproducible free lead results could be achieved with a range of  $\pm 0.3\%$ .

The mill operator results revealed that their inability to perform the titration procedure accurately could be the factor which was responsible for the previously observed free lead variations in Chapter One (Figure 1(iii)).

If the free lead property was to continue being routinely measured by the oxide mill operators to assess the quality of freshly produced lead oxide powder, a new experimental procedure would have to be introduced which required less analytical skill than the titration procedure. The introduction of such a procedure could enable the oxide mill operators to routinely achieve consistent reproducible free lead results. The acetic acid procedure was considered the ideal choice because the end point of the original titration method was difficult to determine with any degree of precision.

The senior management within the company considered



the traditional acetic acid procedure (although extensively used throughout the other lead acid battery companies within the Yuasa Corporation Group) to have a high analytical chemistry content for oxide mill operators with no laboratory technician experience.

As a result a modified acetic acid procedure was developed during this work. It involved weighing a sample of lead oxide (5 g) into a glass crucible (volume 60 cm<sup>3</sup>, porosity number 4). The crucible fits into a buchner flask using a crucible adapter. 20 cm<sup>3</sup> of a 1:3 (by volume) glacial acetic acid solution was poured over the lead oxide powder. A vacuum sucked the acetic acid through the powder. The residue of free lead in the crucible was washed three times with deionised water (3 x 60 cm<sup>3</sup>) and once with industrial methylated spirit (IMS) (60 cm<sup>3</sup>). Washing through with IMS removed water, which ensured that the residue could be dried at a low oven temperature (70 to 80°C). (The original method dried at the higher temperature of 130°C. It was thought that the higher temperature could cause some of the lead residue to oxidise which would effect the accuracy of the free lead measurement). The residue was dried to constant weight. This was usually achieved within ten minutes. Equation 3(vi) represents the calculation used to determine the

content of free lead.

Equation 3(vi)

$$\text{Content of free lead} = \frac{\text{Wt. of dried residue}}{\text{Wt. of sample}} \times 100$$

For the new acetic acid procedure to replace the existing titration procedure, it had to prove that it was capable of producing accurate, reproducible free lead results. To prove this, samples were collected over a period of one month and both the acetic acid and titration procedures were performed on each individual sample. The titration procedures were performed by myself and the laboratory technicians. The first twenty were performed by the laboratory technicians and the remainder were performed by myself. The acetic acid procedures were performed by myself, the operators and the laboratory technicians. The first fifteen were performed by the operators, the next fifteen were performed by the laboratory technicians and the remainder were performed by myself. Table 3(vi) summarises the results.

**Table 3(vi) - Comparison of free lead data measured using both the acetic acid and titration experimental procedures**

Sample Number	Free Lead Content Determined By The Acetic Acid Method		Range	Mean Free Lead Content	Free Lead Content Determined By The Titration Method	Range	Mean Free Lead Content	Percentage Difference Between Means
	%		%	%	%	%	%	%
1	19.9	19.6	0.3	19.8	22.6	0.7	22.1	2.3
	19.8				21.9			
					22.0			
2	20.1	19.8	0.3	19.9	21.9	0.6	22.2	2.3
	19.9				22.1			
					22.5			
3	21.5	21.9	0.4	21.7	24.4	0.6	24.1	2.4
	21.7				23.8			
					24.2			
4	22.8	23.1	0.3	22.9	25.2	0.5	25.3	2.4
	22.9				25.7			
					25.0			
5	18.8	18.9	0.4	18.7	20.9	0.7	21.0	2.3
	18.5				21.5			
					20.8			
6	21.8	21.5	0.3	21.7	23.7	0.6	23.9	2.2
	21.8				23.9			
					24.3			
7	18.6	18.9	0.3	18.8	20.0	0.7	21.0	2.2
	18.9				22.2			
					20.7			
8	20.2	20.5	0.3	20.3	22.3	0.6	22.3	2.0
	20.3				22.0			
					22.6			
9	20.1	19.8	0.3	20.0	21.6	0.6	22.2	2.2
	20.0				22.2			
					21.9			
10	18.1	18.5	0.4	18.3	20.7	0.7	20.3	2.0
	18.2				20.3			
					20.0			
11	23.2	23.5	0.3	23.4	25.9	0.6	25.6	2.2
	23.4				25.3			
					25.6			
12	22.3	22.7	0.4	22.5	24.6	0.7	24.6	2.1
	22.5				24.2			
					24.9			
13	22.4	22.5	0.3	22.5	24.2	0.7	24.5	2.0
	22.7				24.9			
					24.4			
14	23.1	22.8	0.3	22.9	25.1	0.6	25.4	2.5
	22.9				25.7			
					25.3			
15	21.5	21.9	0.4	21.7	23.8	0.6	23.7	2.0
	21.7				23.4			
					24.0			
16	21.9	21.6	0.3	21.8	24.0	0.6	23.8	2.0
	21.8				23.4			
					23.9			
17	20.3	20.0	0.3	20.2	22.0	0.7	22.3	2.1
	20.2				22.7			
					22.3			

**Acetic Acid Procedure**

1-15 Performed by process operators      16-30 Performed by laboratory technicians

31-35 Performed by myself

Sample Number	Free Lead Content Determined By The Acetic Acid Method %	Range %	Mean Free Lead Content %	Free Lead Content Determined By The Titration Method %	Range %	Mean Free Lead Content %	Percentage Difference Between Means %
18	20.7 20.9 20.5	0.4	20.7	23.0 22.4 22.7	0.6	22.7	2.0
19	19.9 20.1 20.2	0.3	20.1	22.1 22.7 22.4	0.6	22.4	2.3
20	20.1 20.5 20.3	0.4	20.3	22.2 22.8 22.5	0.6	22.5	2.2
21	21.6 22.0 21.8	0.4	21.8	23.9 24.5 23.7	0.6	24.0	2.2
22	21.3 21.6 21.6	0.3	21.5	23.6 23.9 24.3	0.7	23.9	2.4
23	24.2 24.4 24.7	0.3	24.4	26.6 26.9 27.2	0.6	26.9	2.5
24	23.5 23.8 23.9	0.4	23.7	25.8 26.0 26.5	0.7	26.1	2.4
25	21.6 21.9 21.8	0.3	21.8	23.8 23.9 24.4	0.6	24.0	2.2
26	19.9 21.2 21.2	0.3	20.8	22.8 23.5 23.1	0.7	23.1	2.3
27	21.4 21.1 21.2	0.3	21.2	23.0 23.8 23.4	0.8	23.4	2.2
28	21.8 21.5 21.7	0.3	21.7	23.6 24.2 23.9	0.6	23.9	2.2
29	22.5 22.1 22.3	0.4	22.3	24.4 25.0 24.8	0.6	24.7	2.4
30	21.4 21.7 21.4	0.3	21.5	23.5 24.2 23.7	0.7	23.8	2.3
31	23.1 22.7 22.9	0.4	22.9	24.9 25.6 25.4	0.7	25.3	2.4
32	23.5 23.2 23.3	0.3	23.3	25.4 25.9 25.2	0.7	25.5	2.2
33	25.7 26.0 25.8	0.3	25.8	27.9 28.2 28.6	0.7	28.2	2.4
34	26.2 26.6 26.5	0.4	26.4	28.4 28.2 28.8	0.6	28.5	2.1
35	25.9 26.2 25.9	0.3	26.0	27.8 28.5 28.3	0.7	28.2	2.2

#### Titration Process

1-20 Performed by laboratory technicians

21-35 Performed by myself  
Table 3(vi)

Three acetic acid and titration tests were performed on each individual sample. The means and ranges of both tests were compared to determine which had the best reproducibility. Analysis of the data revealed that the acetic acid test was capable of producing results with small variation. The range for consecutive free lead determinations on individual samples was approximately 0.3 to 0.4% compared to 0.6 to 0.7% for the titration results.

The new method for measuring free lead was demonstrated to be capable of obtaining good reproducibility. It was clearly shown that the oxide mill operators were capable of performing the acetic acid procedure to produce results with the same reproducibility as the laboratory technicians and myself.

Further analysis of the results revealed that the mean free lead values for both tests had an apparent difference of 2%. The titration method consistently gave the higher results.

Although the acetic acid procedure produced results which were 2% lower, they were considered to be useful since they displayed far less variation than the previous method. To be able to determine the reason for the consistent 2% variation between the

two experimental procedures was considered to be a whole new research area in itself, the investigation of which would divert attention from the main aims of the project. Perhaps for a future research project, the 2% variation could be investigated. Two possible areas of research to look at would be the amount of material being dissolved by the buffer or the acetic acid solution and the formation of a non-stoichiometric oxide at the material/solution interface. For this research project, the aim was to find a measurement technique which is capable of producing consistent results.

The acetic acid procedure was the same procedure which was used throughout all the sealed lead/acid companies within the Yuasa Corporation. If the acetic acid procedure had not already proved that it was simple to perform and capable of producing consistent reproducible free lead results, it would not be the main experimental procedure used within the Yuasa Corporation for measuring free lead. Hence, the modified acetic acid procedure was chosen as the new procedure for measuring the free lead property. Although free lead values determined by the acetic acid procedure are 2% less than the free lead values determined by the titration procedure, the specification setpoint was not immediately changed from 20-28% to 18-26%. The reason for this was that

the correct free lead value was to be optimised in later work (optimisation of free lead is described in some detail in Chapter Five).

As a result of the introduction of the acetic acid procedure, free lead could again be considered as the property being routinely measured to assess the quality of freshly produced lead oxide powder.

### 3.4 APPARENT DENSITY

The apparent density property can be measured on a routine basis to assess the quality of freshly produced lead oxide. It is an important property to monitor and control due to the role it has during the formation of active material. Apparent density is a rough estimate of particle size distribution which determines the internal surface of the active material. The recommended apparent density specification is 0.95 to 1.25 g/cm<sup>3</sup>. If lead oxide can be produced with the apparent density property within its specification limits, it can be assumed to be of acceptable quality for use in production of battery paste. Samples of lead oxide powders with low apparent density values (0.95 to 1.05 g/cm<sup>3</sup>) consist predominantly of large particles, whereas samples of lead oxide powders with high apparent density values (1.20 - 1.25 g/cm<sup>3</sup>) consist

predominantly of small particles.

#### 3.4.1 THE EXPERIMENTAL PROCEDURE FOR MEASURING APPARENT DENSITY

The procedure involves sieving approximately 100 g of sample through a wire mesh (wire diameter 0.274 mm and aperture 0.784 mm) housed in a conical funnel. The sieving action is achieved by filling a hollow tube and moving it in a clockwise direction over the mesh surface. The lead oxide powder collects in a receptacle of known volume, which is weighed when full. The weight corresponds to the apparent density of the lead oxide powder sample.

The time involved in collecting the quantity of lead oxide powder to perform an apparent density test had resulted in the test becoming less frequently used. It was no longer used as a routine test for assessing the quality of freshly produced lead oxide powder but was now only performed once a week. Far more emphasis was placed on measuring free lead.

If apparent density was to be reintroduced as one of the routine production control quality tests for assessing lead oxide quality, it would have to be proved that it was capable of reproducible results.



#### 3.4.2 TESTS TO ASSESS THE REPRODUCIBILITY OF THE APPARENT DENSITY EXPERIMENTAL PROCEDURE

Apparent density tests were performed on the same samples by myself, the oxide mill operators and laboratory technicians. For each sample, three apparent density tests were performed. The mean and range values of the operator results were compared with the measurements obtained by myself and the laboratory technicians. The results are shown in Figure 3(vii). The first ten samples were analysed by the laboratory technicians, whereas the remainder were analysed by myself. The oxide mill operators analysed all the samples.

**Table 3 (vii) Analysis of apparent density data measured by myself, the oxide mill operators and laboratory technicians**

Sample number	Apparent density values measured by the oxide mill operators (g/cm <sup>3</sup> )	Range (g/cm <sup>3</sup> )	Mean apparent density (g/cm <sup>3</sup> )	Apparent density values measured by both myself and laboratory technicians (g/cm <sup>3</sup> )	Range (g/cm <sup>3</sup> )	Mean apparent density (g/cm <sup>3</sup> )
1	1.2 1.19 1.19	0.01	1.19	1.2 1.19 1.2	0.01	1.2
2	1.14 1.13 1.15	0.02	1.14	1.14 1.14 1.15	0.01	1.14
3	1.11 1.1 1.1	0.01	1.1	1.1 1.11 1.1	0.01	1.1
4	1.15 1.15 1.16	0.01	1.15	1.16 1.16 1.15	0.01	1.15
5	1.16 1.17 1.16	0.01	1.16	1.17 1.16 1.16	0.01	1.16
6	1.2 1.2 1.2	0	1.2	1.2 1.2 1.19	0.01	1.2
7	1.14 1.13 1.14	0.01	1.14	1.14 1.14 1.14	0	1.14
8	1.09 1.1 1.09	0.01	1.09	1.1 1.09 1.09	0.01	1.09
9	1.14 1.14 1.15	0.01	1.14	1.15 1.15 1.14	0.01	1.15
10	1.19 1.19 1.19	0	1.19	1.19 1.19 1.19	0	1.19
11	1.2 1.19 1.19	0.01	1.19	1.19 1.19 1.2	0.01	1.19
12	1.14 1.15 1.14	0.01	1.14	1.15 1.15 1.14	0.01	1.15
13	1.16 1.16 1.15	0.01	1.16	1.15 1.16 1.16	0.01	1.16
14	1.11 1.11 1.11	0	1.11	1.11 1.11 1.11	0	1.11
15	1.13 1.12 1.12	0.01	1.12	1.12 1.12 1.12	0	1.12
16	1.09 1.09 1.08	0.01	1.08	1.08 1.08 1.09	0.01	1.08
17	1.14 1.13 1.13	0.01	1.13	1.13 1.13 1.14	0.01	1.13
18	1.15 1.15 1.15	0	1.15	1.14 1.15 1.15	0.01	1.15
19	1.19 1.18 1.18	0.01	1.18	1.19 1.19 1.19	0	1.19
20	1.1 1.11 1.11	0.01	1.11	1.11 1.11 1.1	0.01	1.11

Table 3(vii)

Comparison of the apparent density measurements revealed no variation. Hence the oxide mill operators proved capable of using the apparent density procedure for producing reproducible results. The apparent density property proved that it could once again be used as one of the production control tests for assessing the quality of freshly produced ball mill lead oxide powder.

Additional apparent density measurements were routinely performed over a period of one month to enable the oxide mill operators to get used to routinely using the procedure (The test had dropped out of favour because the oxide mill operators believed that it was too time consuming). Three measurements on each individual sample were carried out. Table 3(viii) reveals the results. The first ten samples were analysed by the oxide mill operators whereas the remainder were analysed by the laboratory technicians.

Table 3 (viii) Apparent density data collected over a one month period

Sample number	Apparent density measurements (g/cm <sup>3</sup> )	Mean apparent density (g/cm <sup>3</sup> )
1	1.13 1.13 1.12	1.13
2	1.13 1.13 1.12	1.13
3	1.12 1.11 1.12	1.12
4	1.13 1.14 1.14	1.14
5	1.14 1.13 1.14	1.14
6	1.12 1.13 1.13	1.13
7	1.16 1.15 1.15	1.15
8	1.12 1.12 1.11	1.12
9	1.11 1.10 1.11	1.11
10	1.11 1.11 1.11	1.11
11	1.09 1.10 1.10	1.10
12	1.11 1.11 1.10	1.11
13	1.12 1.11 1.12	1.12
14	1.12 1.12 1.12	1.12
15	1.13 1.14 1.14	1.14

Sample Number	Apparent density measurements (g/cm <sup>3</sup> )	Mean apparent density (g/cm <sup>3</sup> )
16	1.11 1.10 1.11	1.11
17	1.12 1.13 1.13	1.13
18	1.14 1.15 1.15	1.15
19	1.16 1.16 1.15	1.16
20	1.15 1.15 1.14	1.15
21	1.17 1.17 1.17	1.17
22	1.18 1.18 1.17	1.18
23	1.17 1.18 1.18	1.18
24	1.21 1.22 1.21	1.21
25	1.19 1.18 1.19	1.19

Table 3 (viii)

Analysis of the results revealed little variation. The data showed a trend from middle to top specification range, which indicated that the oxide mill for the duration of the month was producing lead oxide with predominantly small particle sizes. The range for the data was from 1.10 to 1.21 g/cm<sup>3</sup> which was well within the recommended specification range and could be assumed to be of acceptable quality for use in pasting. The apparent density variation was considered to be due to fluctuations in the oxide mill process conditions. No problems were reported during the month's trial and as a result measurement of the apparent density property was re-introduced as one of the production tests for routinely assessing the quality of freshly produced lead oxide powder.

### 3.5 ACID ABSORPTION NUMBER

The acid absorption number has the potential for being routinely used for assessing the quality of freshly produced lead oxide powder. The acid absorption number is a calculated value obtained from an analytical test. It provides a rough indication of the surface area and porosity of lead oxide (the paste making properties of lead oxide). The recommended specification range of lead oxide acid absorption is 90 to 160 mg of H<sub>2</sub>SO<sub>4</sub> per gram of lead oxide. A high number indicates a fine particle size,

whereas a low acid absorption number indicates coarse particle sizes.

### 3.5.1 THE EXPERIMENTAL PROCEDURE USED FOR DETERMINING ACID ABSORPTION NUMBERS

To determine an acid absorption number requires an acid-base titration to be performed. The titration procedure involves adding a sample of lead oxide powder (10 g) into a sample bottle of volume 200 cm<sup>3</sup>. To this is added 1.4 specific gravity sulphuric acid (50 cm<sup>3</sup>) at a constant rate from a burette. The resulting mixture is shaken for thirty seconds and allowed to stand for five minutes. A slurry is formed which requires filtering to enable it to be titrated against sodium carbonate solution.

### 3.5.2 TESTS TO ASSESS THE REPRODUCIBILITY AND SIMPLICITY OF THE ACID ABSORPTION PROCEDURE

For the acid absorption test to be considered as a potential production control test for assessing the quality of freshly produced lead oxide powder, the experimental procedure would have to be capable of reproducible results and be straightforward for operator use.

To determine this, acid absorption tests were

performed on same samples of lead oxide by myself, the oxide mill operators and laboratory technicians. The three sets of results were compared. Table 3(ix) reveals the results which were obtained. The oxide mill operators analysed all the samples. The first ten samples were analysed by myself whereas the remainder were analysed by the laboratory technicians.

Three acid absorption tests were performed on each sample. The mean and range for each sample was calculated. Comparison of the different groups of data revealed that considerable variation between consecutive readings for individual samples had occurred. It was evident that the procedure appeared incapable of producing consistent results.

As a result of the limitations in the acid absorption experimental procedure, the property was not considered as a possible production control test for assessing the quality of freshly produced ball mill lead oxide powder.



Table 3(a) Analysis of acid absorption data measured by itself, the oxide mill, paceters and laboratory technicians

Sample number	Acid absorption numbers measured by itself oxide mill (mg sulphuric acid/g lead oxide powder)	Range (mg sulphuric acid/g lead oxide powder)	Mean acid absorption number (mg sulphuric acid/g lead oxide powder)	Acid absorption numbers measured by both myself and laboratory technicians (mg sulphuric acid/g lead oxide powder)	Range (mg sulphuric acid/g lead oxide powder)	Mean acid absorption number (mg sulphuric acid/g lead oxide powder)
1	136 121 101	43	119	108 117 93	18	108
2	93 136 111	43	113	130 145 114	31	130
3	107 152 139	45	112	102 119 133	31	110
4	124 111 94	30	110	119 140 128	21	129
5	120 145 92	53	119	110 91 129	38	110
6	116 106 142	39	121	90 108 107	30	106
7	115 100 171	58	140	145 122 113	38	124
8	141 100 126	41	122	116 104 129	12	111
9	132 90 106	42	109	100 118 124	29	115
10	130 182 148	52	153	99 111 150	25	111
11	112 112 124	50	112	130 140 130	20	140
12	110 123 90	33	107	132 128 143	15	134
13	151 178 202	51	177	125 142 112	38	123
14	118 110 146	36	124	94 104 126	18	103
15	152 138 129	41	156	130 143 101	17	135
16	115 129 144	52	129	115 130 145	29	115
17	136 111 92	44	113	113 130 113	32	129
18	90 145 118	55	117	89 129 109	20	109
19	115 129 155	40	131	109 92 118	26	106
20	140 110 105	35	118	122 143 130	21	131

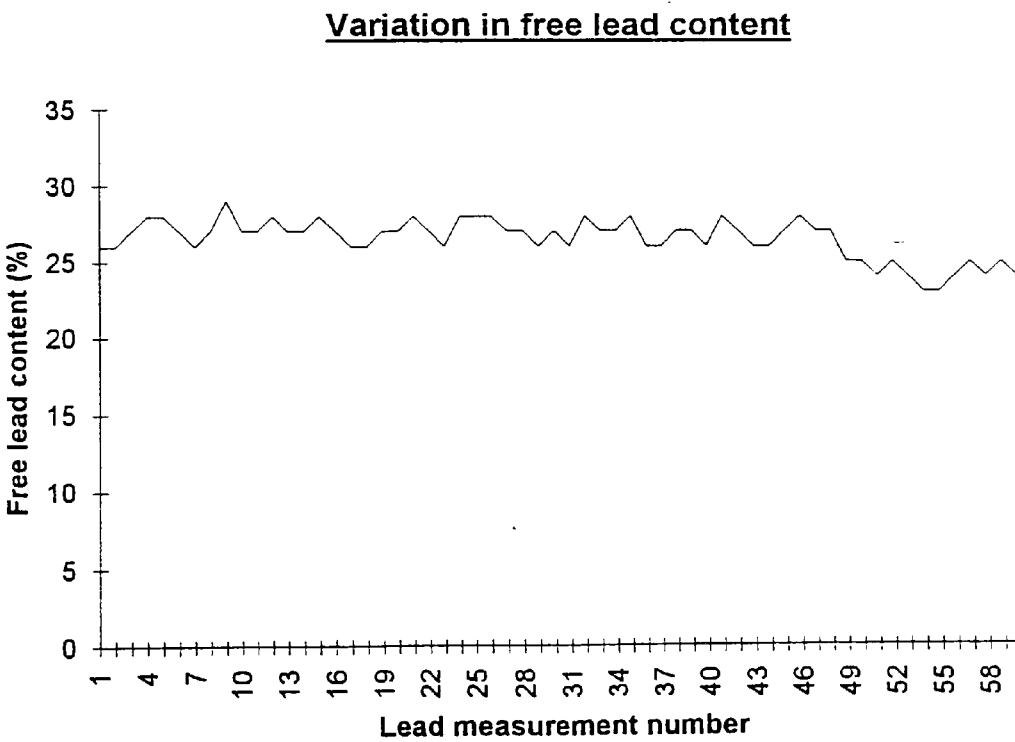
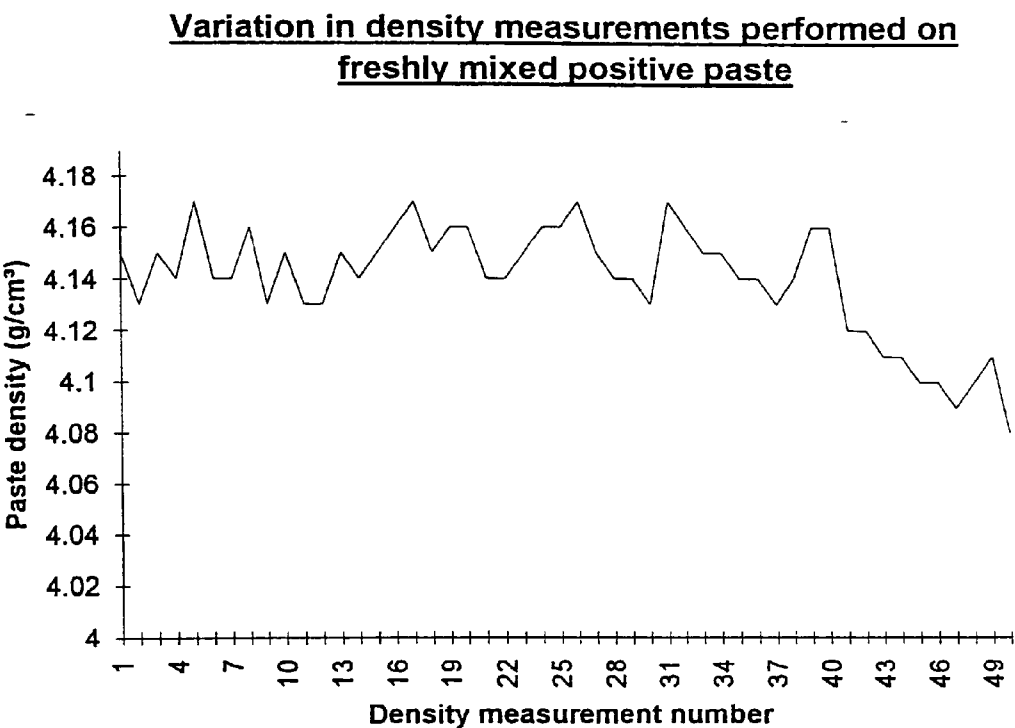
Table 3(a)

### ADDITIONAL MONITORING OF FREE LEAD CONTENT USING THE ACETIC ACID PROCEDURE

After the introduction of the acetic acid procedure for routinely measuring the free lead content of freshly produced lead oxide powder, additional monitoring was performed to determine whether a correlation between free lead content and paste density existed. Twelve production samples were analysed each day for a period of one week. The lead oxide was then followed through to pasting where the density for each paste batch was measured. Over the monitoring period of one week, ten density measurements were performed each day (all free lead content measurements and paste density tests were performed by operators).

Figure 3(iii) represents the comparison of free lead with the paste density data. The results appear to show a trend. The free lead range for four days was 26 to 28% and the corresponding paste density range was 4.13 to 4.17 g/cm<sup>3</sup> whereas on the final day the free lead range was 23 to 25% and the corresponding paste density range was 4.08 to 4.12 g/cm<sup>3</sup>. Also the free lead contents show a much reduced variation compared to the free lead data shown in Figure 1(iii) (Section 1.5).

**Figure 3(iii) Comparison of twelve daily measured free lead contents of freshly produced lead oxide powder which were monitored and followed into ten daily batches of positive paste over a period of one week**



**Fig 3(iii)**

Due to the acetic acid procedure producing reliable results (That is, having removed the random variation due to measurements) the correlation of free lead content with paste density which the company expected was shown to occur. At high range free lead contents (27%  $\pm$  1%) the paste density was high (4.15 g/cm<sup>3</sup>  $\pm$  0.02 g/cm<sup>3</sup>) whereas at medium range free lead contents (23%  $\pm$  1%) the paste density was at the middle specification range (4.10 g/cm<sup>3</sup>  $\pm$  0.02 g/cm<sup>3</sup>). The results demonstrated that the company were correct to claim that lead oxide quality affected paste density.

### 3.7 CONCLUSION

The investigation of the titration experimental procedure revealed limitations which could have been responsible for the majority of the previously observed variations in lead oxide quality. However, before a final conclusion can be given for the exact reason of the previously observed lead oxide quality variations, the effects of the ball mill process variables have to be investigated. After analysis of these results, a final explanation can be given. (See Chapter Four, Section 4.9).

Throughout this phase of the work a number of experimental procedures were examined in an attempt

to find another property which could be routinely used as a production control test for measuring the quality of freshly produced lead oxide powder. The procedures for measuring the particle size and lead oxide colour had the potential to become on line methods for automatically measuring quality. However, both were proved to be unreliable and were not considered capable of being quality control tests. Also the procedure for measuring the acid absorption number was proved to be unreliable and as a result was not considered further.

The existing property for assessing lead oxide consistency was again chosen for use as the quality control test. However, due to the limitations which were discovered with the titration procedure, a new procedure for measuring free lead was introduced; the modified acetic acid method. The new modified procedure proved capable of accurately measuring free lead and was better suited for operator use in the oxide mill environment [The introduction of an experimental procedure which could reliably measure free lead was used to investigate the lead oxide quality required to produce a paste density of  $4.10 \text{ g/cm}^3$  (Section 5.5.1). The measurements which were originally depicted in Figure 1(iii) are unreliable and as a result cannot be used to determine if a correlation between free lead content and paste

density existed. However using the acetic acid procedure, a trend was shown between free lead and paste density (Section 3.6). The introduction of an experimental procedure which could reliably measure free lead was used to investigate the lead oxide quality required to produce a paste density of 4.10 g/cm<sup>3</sup> (Section 5.5.1)].

Also the apparent density property which was a quality control test was chosen to be used for assessing lead oxide quality. The test was originally abandoned by the mill operators because they felt that the procedure was too time consuming to perform. However the investigation of the procedure and the analysis of the results revealed no such problems.

Having completed the investigation into the problems associated with the quality tests, further tests could be performed to determine what effect the ball mill process variables have on lead oxide quality. Additionally, the tests would enable information to be obtained which would help in developing an automated control system, for example data would be obtained showing to what extent certain process variables influence quality. If quality variations were quantified in terms of exact changes in process variables, the results could be used as the basis of an automated control system.

## CHAPTER FOUR

### 4.0      THE EFFECT OF THE OXIDE MILL PROCESS VARIABLES ON LEAD OXIDE QUALITY

The physical process of ball milling lead oxide powder consists of the passage of an airstream through a rotating mill containing approximately 3,500 kg of lead pellets. The tumbling action of the pellets produces small lead particles which oxidise in the airstream. The tumbling motion produces heat which promotes the oxidation of lead. The oxidation reaction is exothermic and this provides more heat to accelerate the process further. The ball mill must be cooled in order to prevent the charge from melting.

The ball mill process has three prime variables. These are:

(i)      Airflow<sup>1,6,8</sup>

This is the air drawn into the ball mill through the lead pellet loading port. Its role is to provide the medium for the oxidation of lead particles and to convey freshly produced lead oxide powder from the ball mill to the filtering cyclones.

(ii) Ball mill temperature<sup>1.6.8</sup>

This is the temperature of the oxidation reaction occurring in the ball mill.

(iii) Ball mill charge level<sup>1.6.8</sup>

The charge level refers to the quantity of lead pellet stock in the ball mill. This property can either be referred to as mill charge or mill level. The charge level occupies the major section of the horizontal air flow plane through the ball mill. This ensures lead particles are constantly available for oxidation.

Two other variables associated with the oxide mill process are air temperature and relative humidity of the air being drawn into the ball mill through the lead pellet loading port. Both variables are suspected of considerable variations over a twenty-four hour period.

4.1 USE OF THE OXIDE MILL PROCESS VARIABLES FOR CONTROLLING LEAD OXIDE QUALITY

The method of controlling the quality of the oxide produced by the ball mill was based on running the



oxide mill process within a set range of operating conditions for air flow, ball mill temperature and level of charge. To help the operators control quality, the oxide mill manufacturers supplied an instruction manual recommending the increments by which the set point conditions for each process variable should be varied under various circumstances.

In order to adjust the air flow set point condition, the fan speed had to be changed by increments of 400 revolutions per minute (rpm). The minimum fan speed was 1,400 rpm whereas the maximum fan speed was 2,760 rpm. If the ball mill was producing lead oxide with low percentage of free lead (lead oxide powder with a content of free lead below 20%) the air flow was increased. If lead oxide with a high content of free lead (greater than 28%) was being produced, the air flow would be decreased. If apparent density was being used to assess lead oxide quality, lowering the air flow would increase apparent density, whereas increasing air flow would decrease the apparent density (Section 4.4.1).

The ball mill temperature was adjusted by increments of 1°C. The minimum temperature at which the process could be operated was 120°C whereas the maximum reaction temperature was 150°C. Adjusting the

setpoint for mill temperature results in only the free lead content varying. Increasing the temperature setpoint results in decreasing the content of free lead, whereas lowering the setpoint temperature increases the content of free lead. No effects on apparent density were known to occur as a result of temperature changes.

The level of mill charge was adjusted by increments of 50 kg. The minimum quantity of charge with which the ball mill could operate was 3,500 kg, whereas the maximum safe charge level was 3,700 kg. If the free lead values are too high during production the level of charge is lowered, whereas increasing the charge level produces lead oxide powder with a higher free lead content.

The above ball mill control concepts were introduced to trainee oxide mill operators by the senior supervisor of the process.

#### 4.2 INVESTIGATION INTO THE RELATIONSHIP BETWEEN OXIDE MILL CONTROLS AND LEAD OXIDE QUALITY

It is hypothesised that variations in the oxide mill process parameters; air flow, charge level and ball mill temperature; could be responsible for some of the previously observed variations in lead oxide quality.

Both ball mill charge level and ball mill temperature were continuously monitored and automatically controlled. However, air flow was not continuously monitored and controlled but instead was manually adjusted by the operators. The air flow through the process was not measured directly but was inferred from the setting of a variable speed fan. Changes in air flow were effected by changing the fan speed.

It was possible for one or more of the process variables to drift from the setpoint values, thus producing the range of lead oxide quality variations observed in Chapter One, Figure 1(iii). Also the lead oxide quality variations could have been caused by fluctuations in the temperature and relative humidity of air drawn into the ball mill through the lead pellet loading port. These variables were neither monitored nor controlled and as such were free to vary unnoticed.

In an attempt to establish whether the previously observed quality variations were, in part, the result of fluctuations in the oxide mill process variables, a series of tests were developed to determine the effect of each process variable on the quality of freshly produced ball mill lead oxide powder. The tests were referred to as steady state sensitivity trials. It was intended that the data obtained from

these tests would be used for developing an automated system for controlling lead oxide production.

#### 4.3 EXPERIMENTAL TECHNIQUE REQUIRED TO DETERMINE THE SENSITIVITY OF EACH OUTPUT TO EACH INPUT

The aim was not to carry out a formal identification of the process plant, but simply to find out which input affects which output and if possible to find out whether there were any dead times involved. The information which was of primary interest was the steady state sensitivity of each output to each input. To achieve this required defined changes to be imposed at a particular point in time (having ensured that all process variables were in steady state before hand) and then to maintain the change for a sufficient length of time to ensure that the full effect of the input had been seen. In addition, time delays between the input being applied and the output change being seen were determined.

Prior to the start of each steady state sensitivity trial, it was determined that the plant had a settling time of about one hour. If a change had occurred to the plant immediately before the trial had started, the one hour period of monitoring the process inputs and outputs would enable the plant to settle back down before the process variable under

investigation was changed from its setpoint condition. The time constant of the response of a plant is defined as that time which it takes a plant to make 63% of the change that it is going to make in infinite time. If using this definition, then good practice indicates that a plant settle down for at least three and preferably five time constants before it can be regarded as fully settled.

In making measurements on plants, it is very important that the correct sampling time is selected. Failure to do so can result in information being lost if the sampling frequency is too low, and an excessive computational work load if too high a frequency is chosen. In order to avoid these pitfalls, some crude preliminary experiments were carried out on the plant. Some preliminary disturbances were imposed on the plant and the time taken for the plant to respond noted. Note was also taken of the speed with which the plant moved under the influence of random noise, this information being used to establish the highest frequency likely to be seen in the output data. The plant operators had claimed that the response time was of the order of one hour. This was taken to mean that all possible changes had eliminated themselves after this period. On this basis, if the plant was linear and first order, one might expect a time constant of the order

of twenty minutes. This was largely borne out by the preliminary experiments. In order to make reasonable measurements, one would normally attempt to take up to ten samples during a time constant, but this would mean taking a sample every two minutes and this was believed to be impracticably fast in the circumstances, since some of the samples had to be manually analysed. In the end, to observe all the changes in lead oxide quality during the steady state sensitivity trial, a sampling interval of five minutes was settled upon, this giving twelve samples during the expected full response time and four during one time constant. This frequency of sampling was far in excess of the routine quality control tests which were performed once every two hours. If changes in lead oxide quality were to occur, the chosen rate of sampling frequency would highlight it. Subsequently, during the experiments, the frequency of sampling was checked against the frequencies appearing in the output trace, and it was verified that several samples were being taken per cycle, thus confirming that the sampling rate was sufficient. Additionally, the plant process variables during each steady state sensitivity trial were monitored at a sampling interval of one minute.

With linear plants, and simple tests such as steady state sensitivity tests, it is important that the

plant is in a steady state prior to being excited by the test signal. To verify this, a time of one hour was allowed before imposing any disturbances and the plant was observed during this time. Assuming no material changes occurred during this time, then the test proceeded. However, had some exterior disturbance occurred during this preliminary hour, the test would have been delayed until a complete hour of steady state behaviour had been observed. This procedure maximises the validity of the results obtained. Once the excitation signal was applied, the plant was allowed to respond and a considerable period allowed to elapse to ensure that all of the response had been seen before applying a reverse step. Typically a period of five hours was allowed to elapse, thus enabling the whole test to be encompassed within a single day shift.

Many of the above rules of thumb are based on the behaviour of linear plants. It was noted that in most industrial plants, this assumption is at best a gross simplification. Unfortunately, due to the amount of noise in the plant, it was necessary to use the maximum excitation signal possible in order to get a clear picture of the response and any attempt to use 50% or 25% disturbances, in order to establish the degree of linearity, would have produced very unreliable results since the response would have been

difficult to identify in the noise. More sophisticated techniques which are resistant to noise were not possible due to the very crude control and actuation mechanisms available for the experiment.

The experimental procedure for each steady state sensitivity test involved subjecting one process variable at a time to a change, whilst the other process variables were kept constant for the duration of the test. For each test, the setpoint conditions for the process variables were set to the lowest values at which they could safely operate. Running the oxide mill with each process variable at its lowest operating setpoint, enabled the maximum change that each process variable could be safely subjected to. The process inputs and outputs were monitored for one hour prior to the change in order to show that the plant was in a steady state. On completion of the first hour, the variable under investigation was subjected to a substantial increase from its setpoint value (100% increase from the setpoint value). The process variable was kept at the new value for five hours, whereupon it was returned to the initial starting value. The process variable was monitored for a further three hours at this condition. No attempt was made to determine whether the sensitivities that were obtained were linear (i.e. if the input change was halved would half the



output response be obtained). Such reduced size stimuli would have so reduced the response that the detailed behaviour would have been lost in the plant noise. Throughout the duration of each test in order to determine the steady state sensitivity of each process variable , both the free lead and apparent density properties were monitored. To help confirm the result of changing each process variable, each test was repeated once.

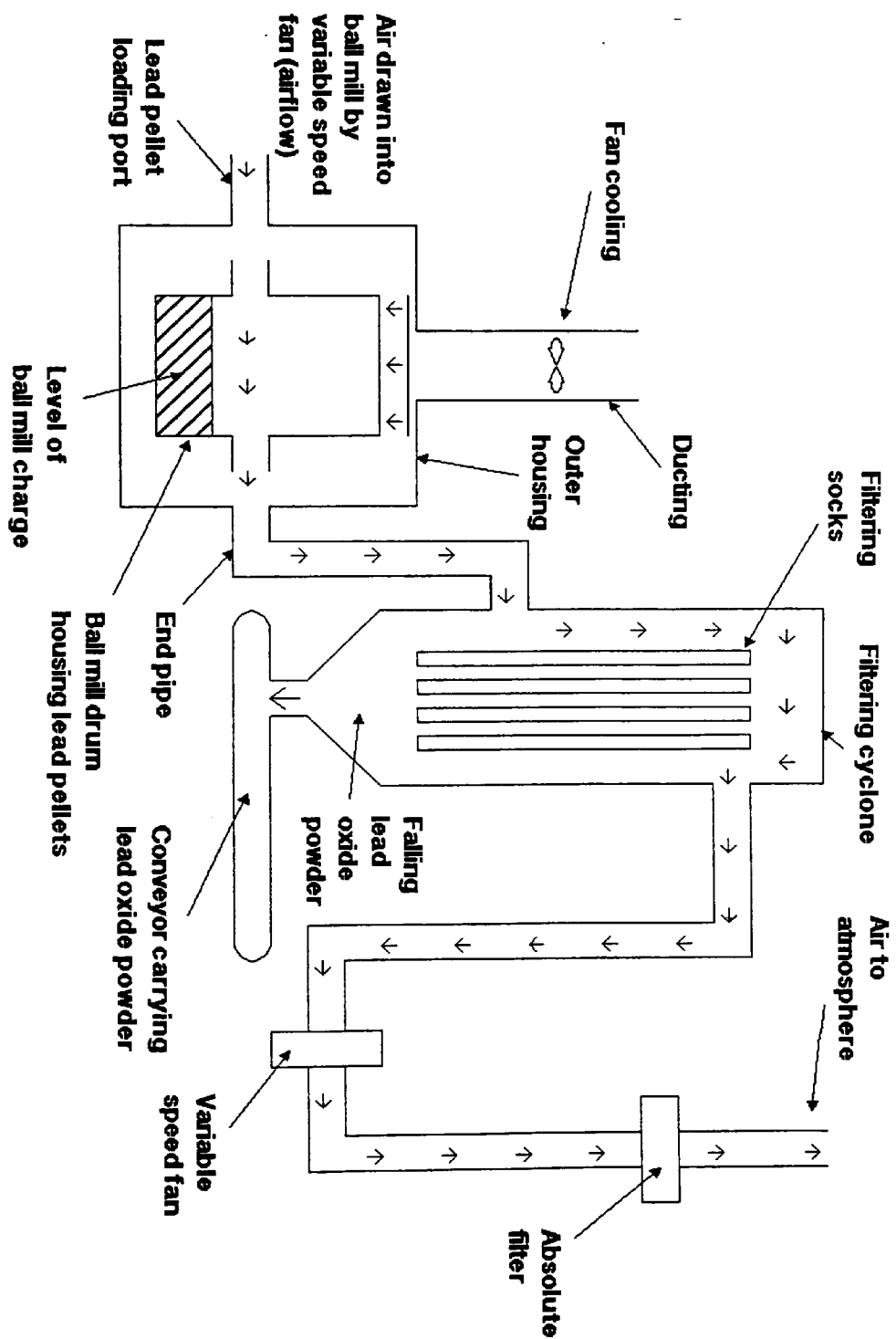
#### 4.4 POSSIBLE VARIATION OF LEAD OXIDE RATE OF PRODUCTION

The factors affecting lead oxide quality would also affect the rate of lead oxide production. To determine if possible production variations were occurring, the lead oxide production rate was continuously monitored throughout each process variable steady state sensitivity test.

However as no facility existed for measuring production rate, a method had to be developed ( Section 4.6.2). Also, in order to perform all the steady state sensitivity tests additional equipment for measuring several of the process variables and methods for varying them were developed ( Section 4.6).

Figure 4(i) represents the ball milling process used for producing lead oxide powder.

**FIGURE 4(i) Lead oxide ball mill process**



*Fig. 4(i)*

The term airflow refers to the air drawn into the ball mill by the variable speed fan. The airflow provides the fuel for the oxidation of lead to lead oxide and also conveys the lead oxide powder from the ball mill to the filtering cyclones. The lead oxide/air mixture enters at the bottom of the filtering cyclone whereupon the lead oxide becomes attached to a series of filtering socks. Pulses of air through the filter socks remove the lead oxide particles which fall to the base of the cyclone. From here the lead oxide particles pass along a screw conveyor to a bucket elevator which conveys them to the lead oxide storage areas at the pasting process. The air now becomes free of lead oxide powder and leaves from ducting at the top of the filtering cyclone. The flow of air finally passes through an absolute filter to remove small traces of lead oxide before being emitted to atmosphere.

Airflow was thought to affect the free lead content and apparent density in the following ways.

FREE LEAD: At low airflows, lead oxide powder remains in the ball mill for a longer period of time and this results in a greater degree of oxidation. This has the effect of producing

lead oxide with a lower percentage of free lead. At high airflows, lead oxide powder remains in the ball mill for a much shorter period of time. This results in less oxidation of the free lead. Hence at high airflows, lead oxide with a higher percentage of free lead is produced.

APPARENT DENSITY: The airflow picks up the various sized particles of lead oxide powder from the ball mill. At low airflows only small particles of lead oxide powder can be transported from the ball mill. This results in producing lead oxide with high apparent densities.

No instrumentation was installed on the ball mill for the measurement of airflow speed. The airflow through the process can be varied by altering the fan speed. However, by not having a valve for airflow through the process, it is possible that airflow variations could be occurring unnoticed.

#### 4.5.2 Ball mill temperature<sup>1,6,8</sup>

The exothermic conversion of lead to lead oxide through the tumbling action of the lead pellet charge and the continuous flow of air through the ball mill

produces considerable heat. The ball mill temperature refers to the temperature of the oxidation reaction. The process produces lead oxide over the ball mill temperature range of 120 to 150°C. The temperature has to be carefully maintained within this band to ensure that no production problems occur.

As with the airflow process variable, ball mill temperature can also be used to control the quality of freshly produced lead oxide powder. The ball mill temperature affects both the free lead and apparent density properties. Increasing the ball mill temperature decreases free lead but increases apparent density whereas decreasing the ball mill temperature increases free lead but decreases apparent density.

Varying the temperature of the oxidation reaction affects the airflow through the mill in addition to (possibly) affecting lead oxide quality. This change in airflow may itself cause changes in free lead and apparent density properties. Changing the ball mill temperature from its setpoint condition produces a change in the volume of air being drawn through the ball mill, even though the speed of the fan has not been altered.

#### INCREASING THE BALL MILL TEMPERATURE:

Decreases the airflow in the ball mill which causes the lead oxide powder to remain for a longer period of time in the ball mill (less airflow for removing it) whereupon the free lead is subjected to more oxidation. A possible explanation for the airflow decrease is that the higher air temperature through the process reduces the fan efficiency, thus leading to a drop in the airflow being pulled through the plant. Due to the decrease in airflow, only small lead oxide particles can be removed from the ball mill and as such the apparent density increases.

#### DECREASING THE BALL MILL TEMPERATURE:

Increases the airflow which results in lead oxide spending less time in the ball mill. As a result the content of free lead increases. However, the increased airflow causes larger lead oxide particles to be removed which results in small apparent density values. Decreasing the plant temperature increases the fan efficiency, thus leading to an increase in the airflow being pulled through the plant.

The ball mill has a control system to ensure that the temperature remains at its setpoint value. The

temperature control procedure involves the use of two temperature instruments which perform on\off control functions. A temperature instrument mounted on the front of the oxide mill control cabinet switches on the cooling fan located above the ball mill (See Figure 4(i)). When the ball mill temperature comes within 2°C of the instrument setpoint of 120°C the fan starts cooling the ball mill. In practice, as the normal operating temperature is 125°C the fan remains on throughout normal operations. The other temperature instrument inside the oxide mill control cabinet was fixed at a setpoint of 130°C. If the ball mill temperature exceeds this setpoint value, a water valve is switched on to continuously douse the surface of the ball mill drum with water. A timer is started when the valve is switched on. If the temperature does not drop below the setpoint value before the time elapses, an alarm sounds and the process shut down procedure is started.

It is possible that the method used for controlling the ball mill temperature could be unreliable and as a result give rise to the previously observed quality variations.

#### 4.5.3 Ball mill charge level<sup>1,6,8</sup>

The level of charge refers to the quantity of lead



pellets in the ball mill. There is a recommended operating range for charge level. The minimum charge level at which the process can be operated is 3,500 kg whereas the maximum charge level at which it can safely operate is 3,700 kg. Varying the charge level between the limits provides a method of controlling the quality of freshly produced lead oxide powder.

INCREASING THE CHARGE LEVEL: Makes it far easier for the airflow to remove lead oxide particles from the ball mill. Hence lead oxide particles remain in the ball mill for a much shorter period of time. This results in lead oxide powder being produced with a higher content of free lead. Increasing the level of charge also has an effect on the apparent density. The raised lead pellet level makes it easier for the airflow to remove the larger lead oxide particles from the ball mill. Thus lead oxide with low apparent density values is produced.

DECREASING THE CHARGE LEVEL: Makes it far more difficult for airflow to remove lead oxide particles from the ball mill. The particles remain in the ball mill for a longer period of time and as a result are subjected to considerably more oxidation which results in

lead oxide with lower contents of free lead. Decreasing the level of charge also affects the apparent density property. The lower charge level makes it more difficult for the airflow to remove particles of lead oxide powder from the ball mill. Therefore, only small particles can be removed which results in the production of lead oxide powder with high apparent density values.

The ball mill process has a system for controlling the level of charge to ensure that it remains at its setpoint value during production. A weighing instrument controls the quantity of lead pellets in the ball mill. When the ball mill weight drops below the lowest setpoint value, lead pellets are fed to the ball mill via the lead pellet loading port. Pellets are fed until the weight is above the instrument's setpoint value. The lower setpoint value is set 10 kg below the upper setpoint value.

It is possible that the method used for controlling the charge level could be unreliable and give rise to the previously observed quality variations.

#### 4.5.4 Air temperature<sup>1,6,8</sup>

The air which is drawn into the ball mill, through

the lead pellet loading port, to fuel the oxidation of lead pellets into lead oxide powder is not conditioned (not controlled at a constant temperature or humidity). The temperature of the fan-drawn air depends on the climatic conditions inside the factory unit. Over a twenty-four hour period of continual production, considerable variations in temperature can occur, which could be influencing lead oxide quality.

Fluctuations in the temperature of air being drawn into the ball mill could effect the quality of freshly produced lead oxide powder by producing variations in the ball mill temperature which in turn would create variations in airflow through the ball mill. Temperature was not measured prior to the investigation, thus no initial opinion on its effect could be reached.

#### 4.5.5 Relative humidity<sup>1,6,8</sup>

The air which takes part in the ball mill oxidation of lead pellets into lead oxide powder contains very small traces of water vapour. The humidity is dependent on the air temperature and is relative to temperature. Relative humidity refers to the water actually present divided by the maximum water possible.

The relative humidity of the fan drawn air depends on the climatic conditions within the factory unit. Over a twenty-four hour period of continual production, considerable variations in relative humidity may occur, which could influence the lead oxide quality.

#### 4.6 ADDITIONAL EQUIPMENT INSTALLED ON THE BALL MILL PROCESS

##### 4.6.1 A probe to measure airflow

A method of measuring airflow through the ball mill process had to be installed. An airflow probe was installed into a region of duct above the absolute filter. This was the only suitable position (the probe could not be positioned in the ball mill end pipe because it would be too difficult to keep it clean). A Trolex T.X. 1329 series airflow probe was chosen because it appeared far more robust than other available airflow measuring techniques. The probe measures airflow in metres per seconds (m/s) over the range of 0.5 to 25 m/s.

##### 4.6.2 Development of a method for measuring the rate of lead oxide production

The system devised to measure the rate at which the

process produced lead oxide powder was based on measuring the quantity of lead pellets being fed into the ball mill. By monitoring the weight of each batch of pellets, the total quantity of pellets fed into the ball mill is known.

The percentage conversion ratio (derived from the relative molecular mass of lead and lead oxide) of lead pellets into lead oxide powder is 1:1.07%, i.e. it can be assumed that for every 100 kg of lead pellets added, approximately 107 kg of lead oxide powder is produced. However, this assumption is not absolutely correct because not all the lead pellets are converted into lead oxide powder. Approximately only 80% of the pellets form lead oxide powder, whilst 20% of the pellets remain as unoxidized lead (Free lead content). Hence the actual rate of production is approximately 86 kg lead oxide and 20 kg of free lead which adds up to 106 kg of product.

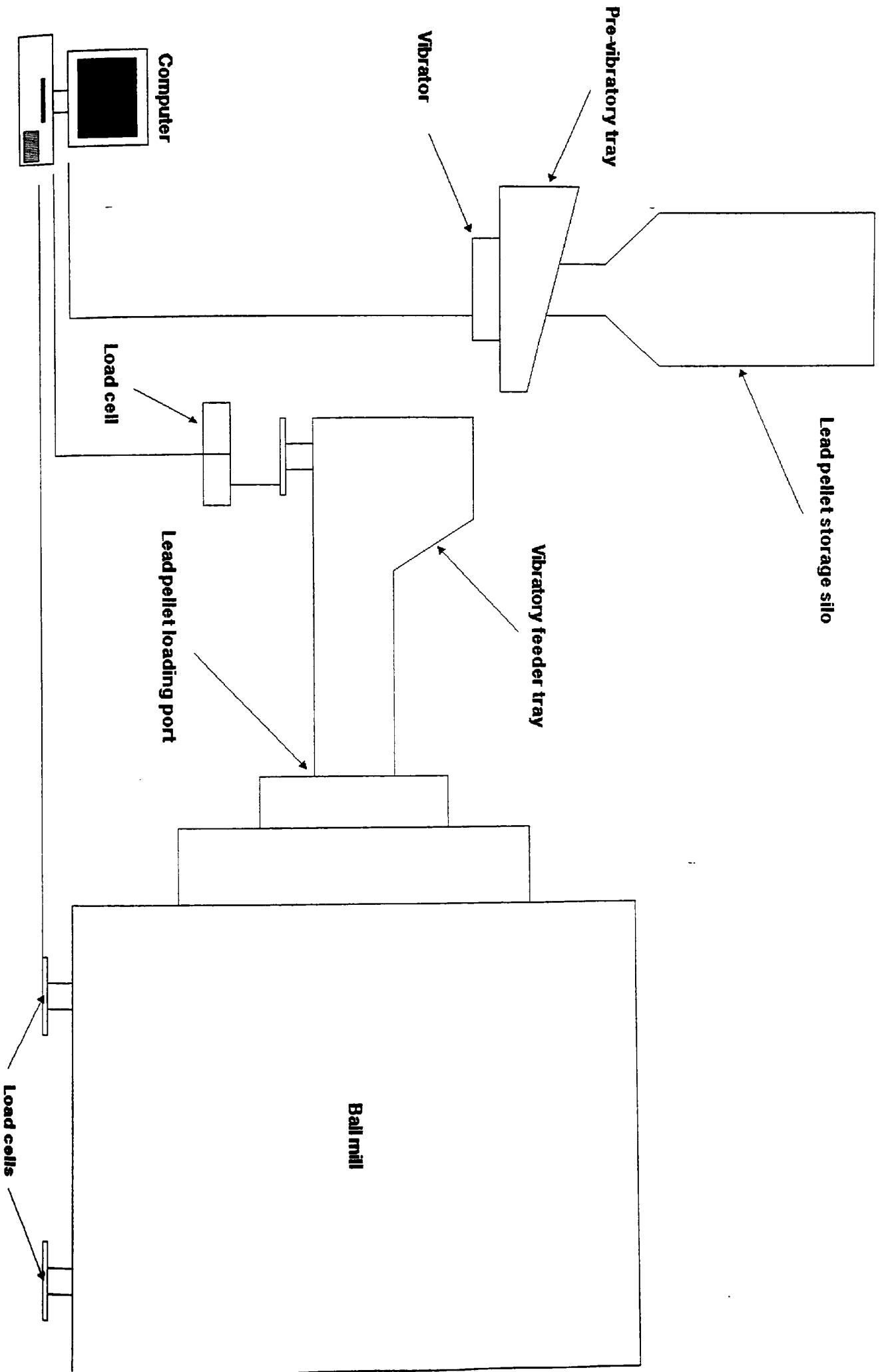
The weight of each shot of lead pellets added to the oxide mill was recorded. Every one hour the total weight of added lead pellets was summed and the percentage conversion carried out. Dividing the value by sixty allowed the production rate to be expressed in kg/min. This was calculated on a rolling basis for each shot added.

The method used a load cell fitted to a vibratory tray feeder with an automatic drive mechanism (the tray was purchased from Riley Automation and therefore became referred to as the Riley tray). A pre-vibrating tray located directly below the lead pellet storage silo was used to rapidly fill the Riley tray. (Figure 4 (ii)).

When the ball mill weight fell below the lower setpoint the system calls for pellets, the pre-vibrating tray vibrates (two second pulses) until the upper setpoint on the Riley tray weighing instrument was reached, indicating 5 kg of pellets on the tray. After a pause of two seconds to allow the monitoring system to record the exact weight of lead pellets, the Riley tray vibrator was started and the lead pellets were fed into the ball mill until the lower (or zero) setpoint on the Riley tray instrument was reached (0.1 kg) at which point the Riley tray stopped vibrating.

By being able to monitor the rate of lead oxide production, the effects of each process variable on it could be determined.

**FIGURE 4(ii) The method for measuring the production rate of lead oxide powder**



**Fig. 4(ii)**

#### 4.6.3 A probe to measure air temperature and relative humidity

A probe was located directly in front of the lead pellet loading port in the ball mill. It was able to measure both the temperature and relative humidity of the air drawn into the ball mill. A Vaisala H.M.P. 130 Y series relative humidity and temperature transmitter was chosen because of Vaisala's history of excellence within the field of relative humidity and temperature measurement. The transmitter measures temperature over the range of -20 to 80°C and relative humidity over the range of 0 to 100%.

#### 4.6.4 Data acquisition equipment

The types of probes and weighing instruments used on the oxide mill process, output the measured process variables as analogue signals. For example, the probe which measures airflow produces a 4 to 20 milliamp (mA) analogue signal which equates to an airflow range of 0.5 to 25 m/s.

Equipment was required which could store and monitor the performance of each process variable during the steady state sensitivity tests. By having an accurate account of each process variables behaviour, correlation with either lead oxide quality or rate of



production could be investigated.

Software driven data acquisition hardware was used which was capable of measuring the process variables to an adequate accuracy under plant conditions where it is noisy. The data acquisition board used was a real-time interface input/output (I/O) board which is compatible with an IBM PC. It is a multi-function data acquisition board that has capabilities for various modes of analogue/digital, input/output operation. The board plugged into one of the available long expansion slots in the IBM PC. The computer program required to monitor the process variables was written by a colleague at Yuasa Battery (U.K.) Ltd with experience in data acquisition.

The process variables measured were airflow, ball mill temperature, ball mill charge level, air temperature, relative humidity and lead oxide production rate.

#### 4.7 THE STEADY STATE SENSITIVITY TESTS

Tests, referred to as steady state sensitivity tests were used to assess which process variables affected the quality and production rate of lead oxide in the ball mill.

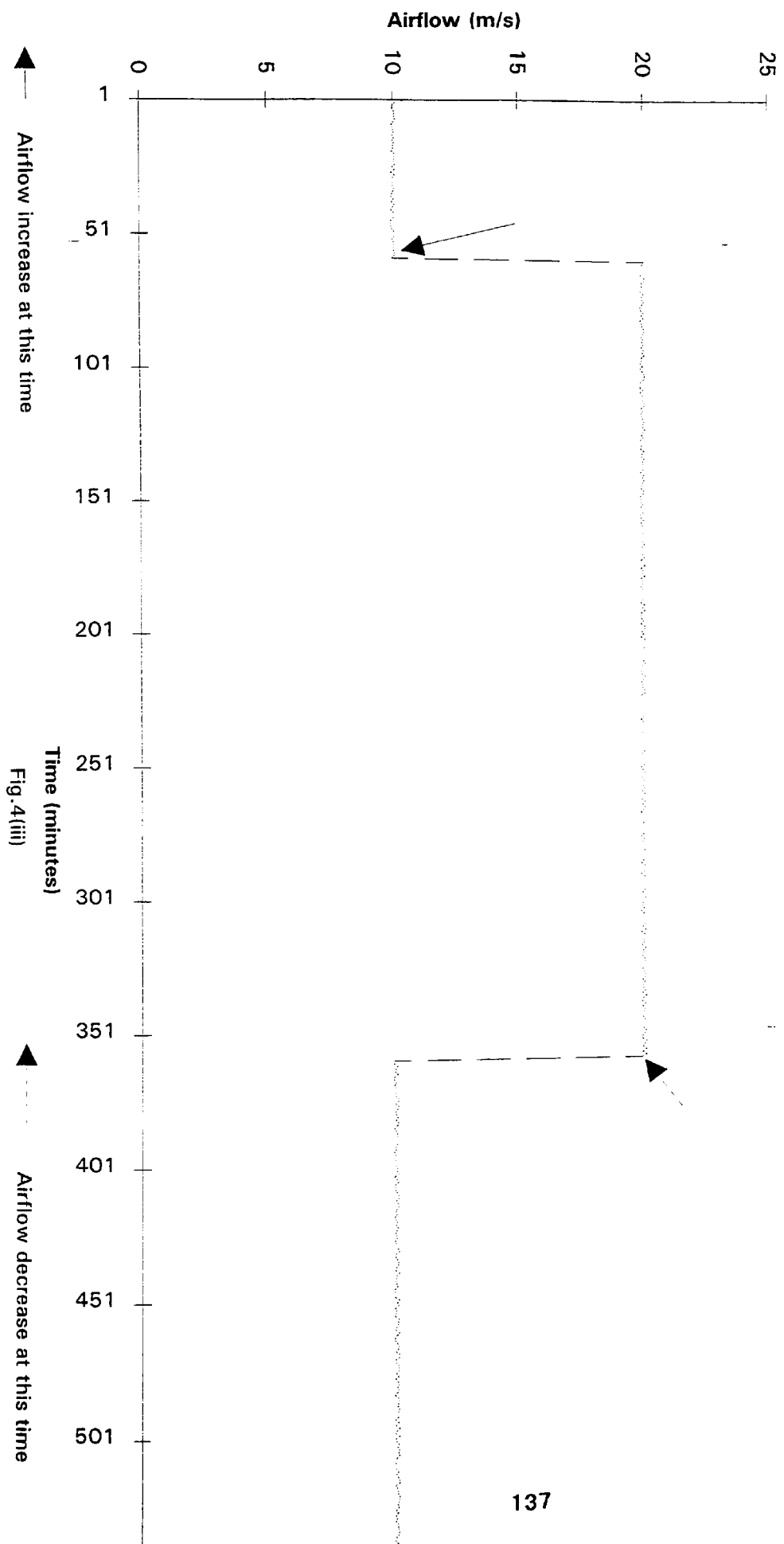
The experimental procedure for each steady state sensitivity test involved subjecting one process variable at a time to a change, whilst the remaining process variables were held constant for the duration of the test (see Section 4.3). For each steady state sensitivity test, both lead oxide quality and rate of production were continually monitored.

#### 4.7.1 AIRFLOW STEADY STATE SENSITIVITY TEST

(See Section 4.3 for details on choice of plant settling times and frequency of process variable and lead oxide quality sampling).

The initial airflow speed through the ball mill process was set at 10 m/s ( $\pm 0.1$  m/s). This was the lowest airflow set point at which the oxide mills could safely operate. After a one hour plant settling period, it was increased to 20 m/s ( $\pm 0.1$  m/s). This was the highest airflow set point which was able to be achieved. The airflow remained at the set point of 20 m/s for five hours. This extended period of time allowed the response for each process output to be fully observed. After five hours, the airflow was returned to its initial speed of 10 m/s ( $\pm 0.1$  m/s) and the plant was monitored for a further three hours (Figure 4(iii)).

**Figure 4(iii) Profile of the airflow steady state sensitivity trial**



Throughout the nine hour trial, the lead oxide rate of production and both the free lead content and apparent density were monitored.

The other oxide mill process variables for the duration of the trial were kept constant at normal operating setpoints. The ball mill temperature was 125°C, the ball mill charge level was 3,500 kg, the relative humidity was 35% and the air temperature was 30°C. For the duration of the steady state sensitivity test, the monitoring frequency for each process variable was one minute.

#### 4.7.1.1. DISCUSSION OF THE AIRFLOW STEADY STATE SENSITIVITY TEST

##### (a) Effect on the other process variables

For the duration of the airflow steady state sensitivity trial, the other process variables were continually monitored to ensure that they remained constant.

##### (i) Ball mill temperature (Figure A(i) Appendix)

The ball mill temperature prior to the airflow change was set at 125°C.

Analysis of Figure A(i) reveals that it remained constant at 125 °C (  $\pm 1^{\circ}\text{C}$  ) over the trial period. The change in air flow had no effect on the temperature within the ball mill.

(ii) Ball mill charge level  
(Figure A(ii) Appendix)

The setpoint for ball mill charge was 3,500 kg. Analysis of Figure A(ii) revealed that the charge level remained constant at 3500 kg (  $\pm 10$  kg ) over the trial period.

(iii) Relative humidity of air entering the ball mill  
(Figure A(iii) Appendix)

Throughout the duration of the trial the relative humidity remained constant at 35% (  $\pm 2\%$  ). This was achieved by constructing a totally enclosed plenum chamber directly in front of the lead pellet loading port. A steady flow rate of steam was allowed to drift at a fixed flow rate into the path of the constructed

chamber by means of an industrial air blower. The industrial blower forced steam to disperse directly in front of the lead pellet loading port. A constant value for relative humidity was maintained using this system. However it must be noted, that this method did not control the actual vapour pressure in the air. Analysis of Figure A(iii) revealed that the relative humidity of air drawn into the ball mill remained constant at 35% (+/- 2%) over the trial period.

(iv) Temperature of air entering the ball mill

(Figure A(iv) Appendix)

Throughout the duration of the trial, the air temperature remained constant at 30°C (+/- 1°C). This was achieved by using a gas heater. The gas heater was positioned at the entrance to a sealed plenum chamber area which was constructed in the area directly in front of the lead pellet loading port. The industrial heater forced

hot air to disperse directly in front of the loading port. The gas heater and the constructed chamber ensured that the temperature of air entering the ball mill remained constant. Analysis of Figure A(iv) revealed that the temperature of air drawn into the ball mill had remained constant at 30°C (+/- 1°C) over the trial period.

(b) Effect on lead oxide quality and rate of production

The time taken to increase the airflow to 20 m/s was one minute. The airflow was also returned to 10 m/s in one minute. The variable speed fan proved capable of producing rapid responses in airflow. The effects on both lead oxide quality and rate of production were as follows:

(i) Free lead content

(Figure 4(iv))

The free lead content prior to the steady state sensitivity trial was 20.3% (+/- 0.3%). Increasing the airflow from 10 to 20 m/s resulted in

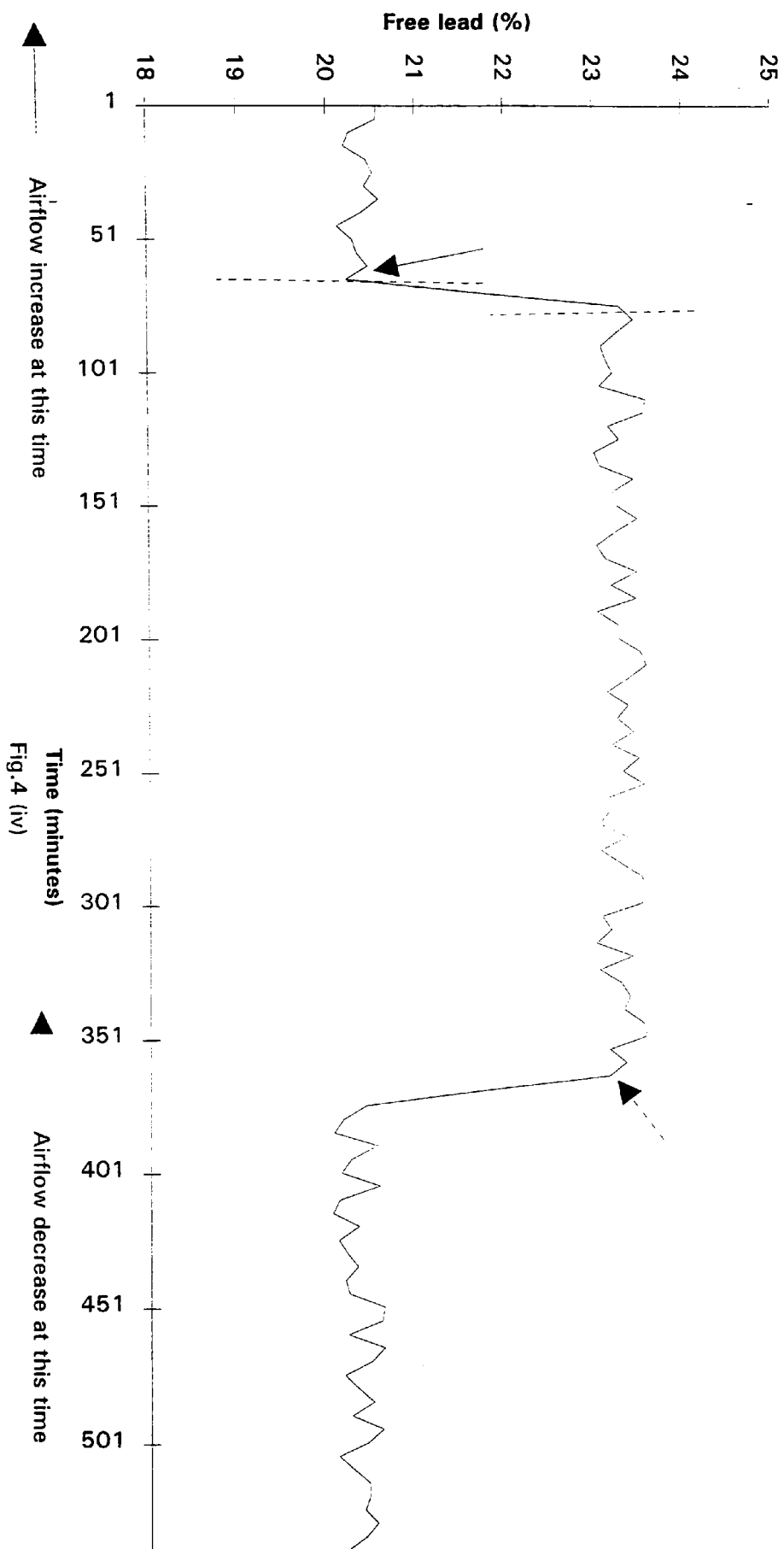
the free lead increasing to 22.7% (+/- 0.3%). The free lead reached this range, fifteen minutes after the airflow was increased. The free lead content remained at the range 22.7% (+/- 0.3%) for the five hour period the airflow was at 20 m/s.

Returning the airflow to 10 m/s resulted in the free lead decreasing to 20.3% (+/- 0.3%). Again the free lead reached this range fifteen minutes after decreasing the airflow. The free lead remained at 20.3% (+/- 0.3%) for the remaining three hours of the trial. The steady state sensitivity was 0.24% per metre/sec with a delay of fifteen minutes.

When the oxide mill operated at the high airflow value of 20 m/s, it resulted in lead oxide powder being removed at a far quicker rate from the ball mill. This resulted in lead oxide powder being subjected to less oxidation within the ball mill and the content of free lead in freshly produced lead oxide powder increased.



**Figure 4(iv) The effect of the airflow steady state sensitivity test on free lead**



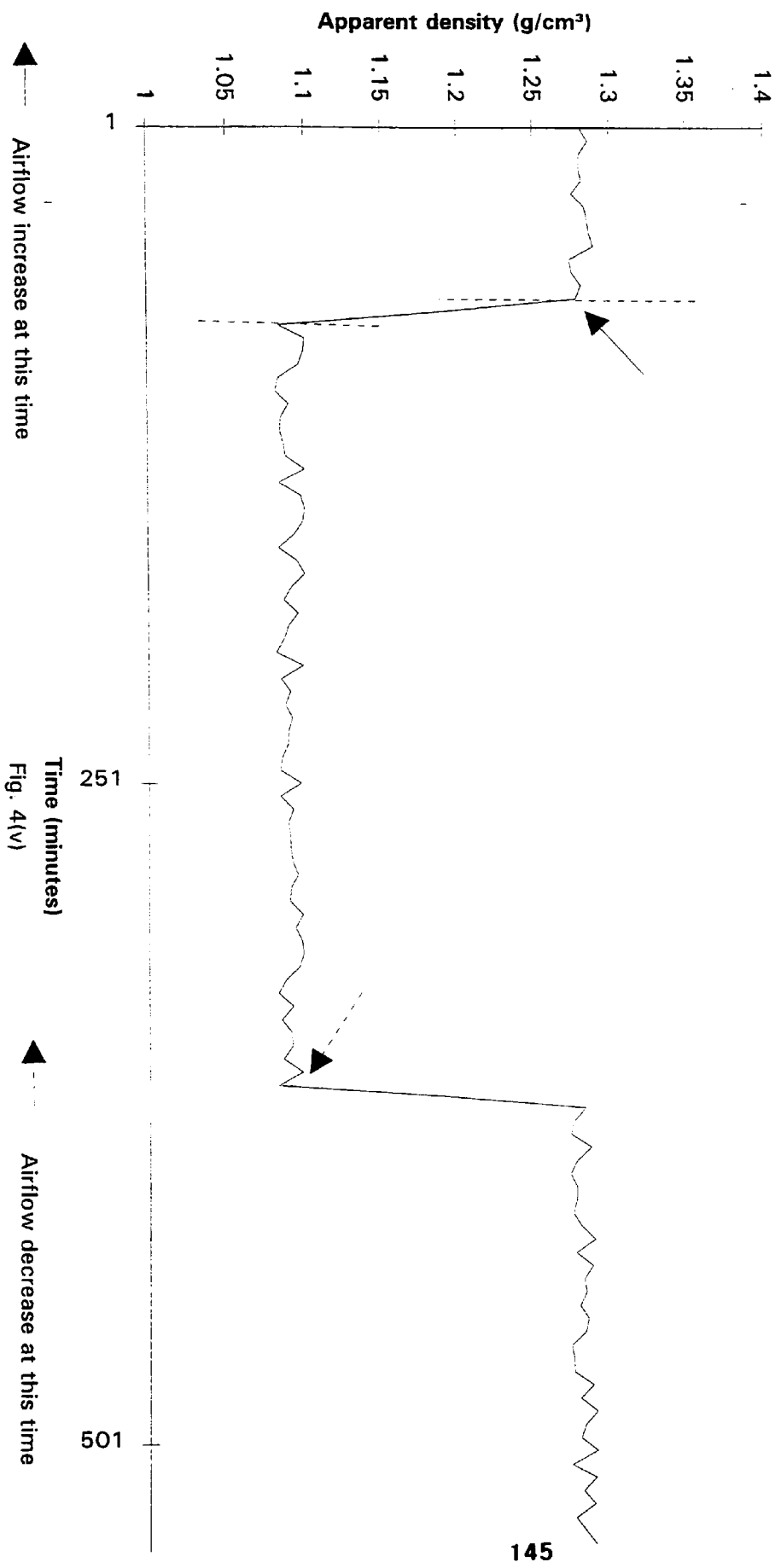
(ii) Apparent density property

(Figure 4(v))

The apparent density prior to the steady state sensitivity trial was constant at  $1.28 \text{ g/cm}^3$  ( $\pm 0.01 \text{ g/cm}^3$ ). When the airflow through the process was increased to 20 m/s, the apparent density of the freshly produced lead oxide powder dropped to  $1.09 \text{ g/cm}^3$  ( $\pm 0.01 \text{ g/cm}^3$ ). The apparent density reached  $1.09 \text{ g/cm}^3$  fifteen minutes after the change in airflow and remained constant at this value for the five hour period while the airflow was at 20 m/s.

Returning the airflow to 10 m/s resulted in the apparent density increasing back to  $1.28 \text{ g/cm}^3$  ( $\pm 0.01 \text{ g/cm}^3$ ). Again the time taken was fifteen minutes. The apparent density remained constant at  $1.28 \text{ g/cm}^3$  ( $\pm 0.01 \text{ g/cm}^3$ ) over the remaining three hours of the trial.

**Figure 4(v) The effect of the airflow steady state sensitivity test on apparent density**



At the low airflow value of 10 m/s, lead oxide particles were less easily removed from the ball mill and as a result, only lighter particles could be removed. The apparent density test procedure allowed small particles to pack closely together which enabled more lead oxide powder to be shaken into the density cup holder. As a result, lead oxide samples had a higher apparent density value at low airflow. The steady state sensitivity was  $-0.019 \text{ g/cm}^3$  per metre/sec with a time delay of fifteen minutes.

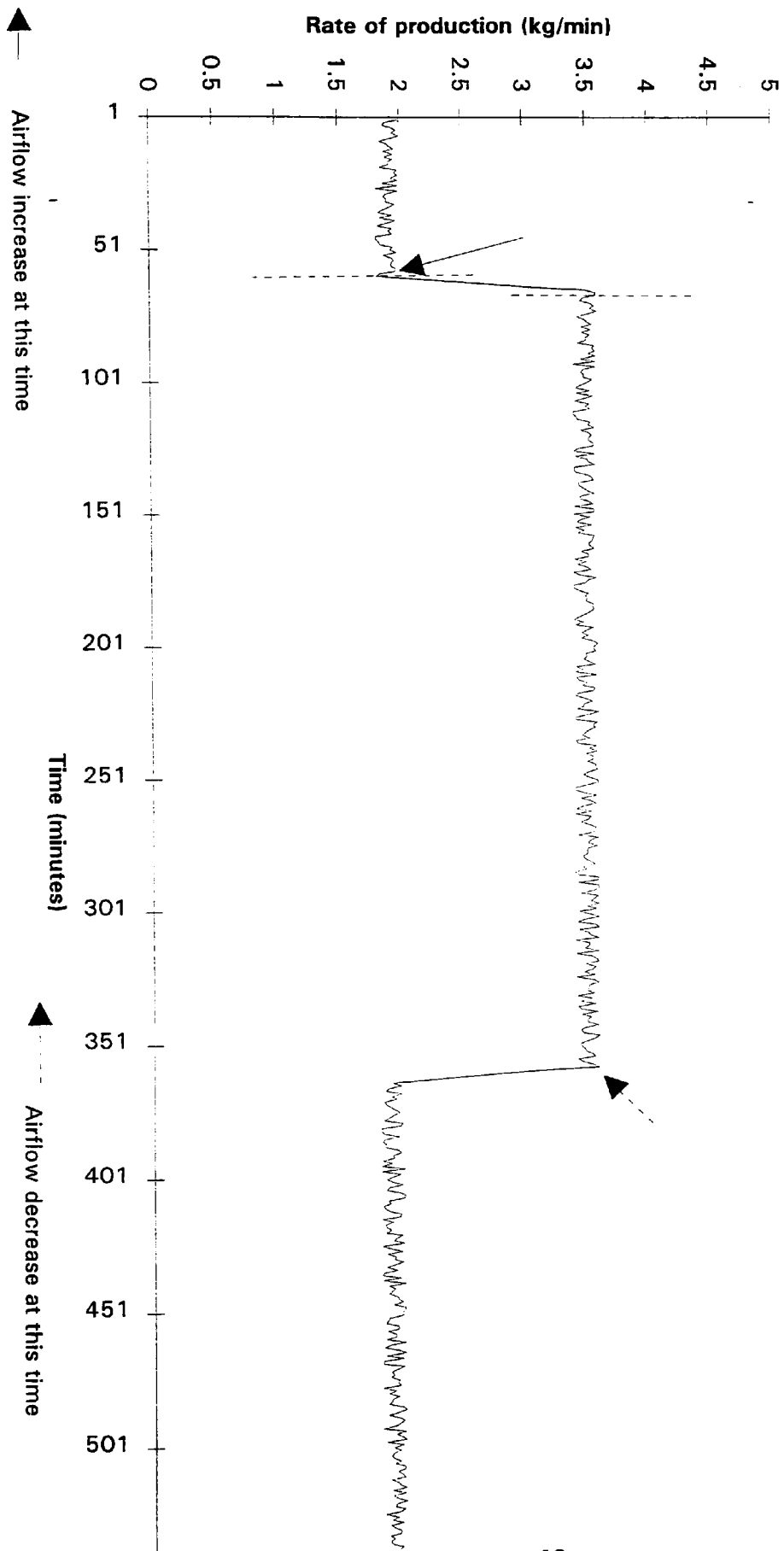
(iii) Rate of production of lead oxide  
(Figure 4(vi))

The lead oxide rate of production prior to the trial was constant at  $1.9 \text{ kg/min}$  ( $\pm 0.1 \text{ kg/min}$ ). When the airflow was increased from 10 to 20 m/s, the production rate of freshly produced lead oxide powder increased to  $3.5 \text{ kg/min}$  ( $\pm 0.01 \text{ kg/min}$ ). The production rate reached  $3.5 \text{ kg/min}$  ( $\pm 0.1 \text{ kg/min}$ ) five

minutes after the airflow was changed. The rate of production remained constant at 3.5 kg/min (+/- 0.1 kg/min) for the five hour period the airflow was at 20 m/s. Returning the airflow to 10 m/s, resulted in the rate of production decreasing back to 1.9 kg/min. Again the time taken was five minutes. The rate of production remained constant at 1.9 kg/min (+/- 0.1 kg/min) over the remaining three hours of the trial. Running the oxide mill at 20 m/s resulted in the lead oxide production rate approximately doubling from 1.9 to 3.5 kg/min (+/- 0.1 kg/min). The company are now reluctant to run the oxide mills at low airflow rates.

At the airflow value of 20 m/s, the higher flow rate carries more material through in a given time. Hence the oxide mill produced lead oxide powder at a high rate of production. The steady state sensitivity was 0.16 kg/min per metre/sec with a time delay of five minutes.

**Figure 4(vi) The effect of the airflow steady state sensitivity test on lead oxide rate of production**



(c) Comparison of the airflow change quality variations (free lead) with the previously observed variations in Chapter One

The production values displayed in Chapter One (Figure 1(iii)) show the free lead values which were determined by the oxide mill operators. The operators measured free lead every two hours. Hence over a twenty-four hour period, twelve titrations had been carried out. The range in free lead values over a day's production was between 19.3 and 27%.

Throughout the airflow steady state sensitivity trial, the free lead contents of lead oxide samples were also measured. However, instead of performing one titration every two hours, twelve titrations were performed each hour. This was the quickest sampling frequency which was practically possible. Hence over the duration of the nine hour trial, one hundred and eight free lead titrations were performed. During the airflow steady state sensitivity trial, the process operators did not perform any of the free lead determinations. All titrations during the trial were performed by trained laboratory staff.

The range in free lead values over the nine hour trial were as follows:

- (i) Prior to the start of the trial, the free lead range was 20.3% (  $\pm$  0.3%).
- (ii) For the five hour period after the change, the free lead range was 22.7% (  $\pm$  0.3%).
- (iii) Returning the airflow change to its original value resulted in free lead returning back to 20.3% (  $\pm$  0.3%).

Comparison of the oxide mill production results in Chapter One with the airflow steady state sensitivity results show that variations in airflow through the oxide mill process were unable to produce percentage changes in free lead of similar magnitude. The airflow results therefore confirms that the production variations in free lead previously reported were not the result of the airflow alone varying uncontrollably but was entirely due to the errors in analysis previously discussed.



#### 4.7.2 BALL MILL TEMPERATURE STEADY STATE SENSITIVITY TEST

The ball mill temperature was initially set at 125°C (+/- 1°C). After one hour, it was increased to 140°C (+/- 1°C). The ball mill temperature was kept at this setpoint for five hours, after which it was returned to its initial value of 125°C (+/- 1°C). The ball mill temperature was monitored at this value for a further three hours (Figure 4(vii)). Throughout the nine hour trial the lead oxide rate of production and the free lead and apparent density were monitored.

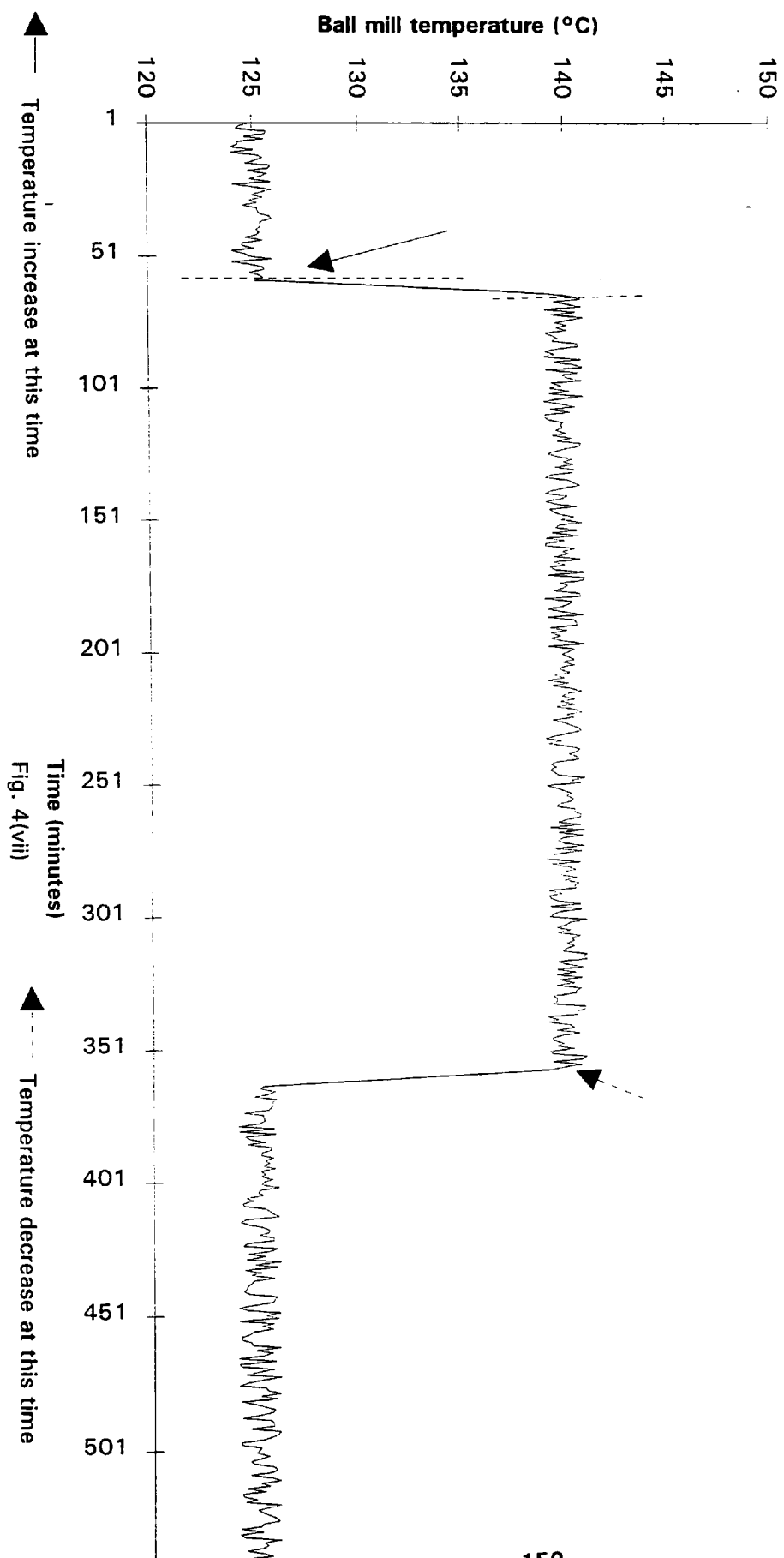
The other oxide mill process variables were also monitored throughout the trial period.

##### 4.7.2.1 DISCUSSION OF THE BALL MILL TEMPERATURE STEADY STATE SENSITIVITY TEST

###### (a) Effect on the other process variables

For the duration of the ball mill temperature steady state sensitivity test, the other process variables were continuously monitored.

**Figure 4(vii) Profile of the ball mill temperature steady state sensitivity trial**



(i) Ball mill charge level

(Figure A(v) Appendix)

At the start of the trial, the setpoint for the ball mill charge level was 3,500 kg. Analysis of Figure A(v) revealed that it remained constant at 3500 Kg (+/- 10 kg) over the trial period.

(ii) Relative humidity of air entering the ball mill

(Figure A(vi) Appendix)

The steam line was set up at the start of the trial to ensure that the relative humidity directly in front of the ball mill was 35%.

Analysis of Figure A(vi) revealed that the relative humidity of air drawn into the ball mill remained constant at 35% (+/- 2%) over the trial period.

(iii) Temperature of air entering the ball mill

(Figure A(vii) Appendix)

The gas heater was set up at the

start of the trial to produce an air temperature of 30°C in the area directly in front of the ball mill.

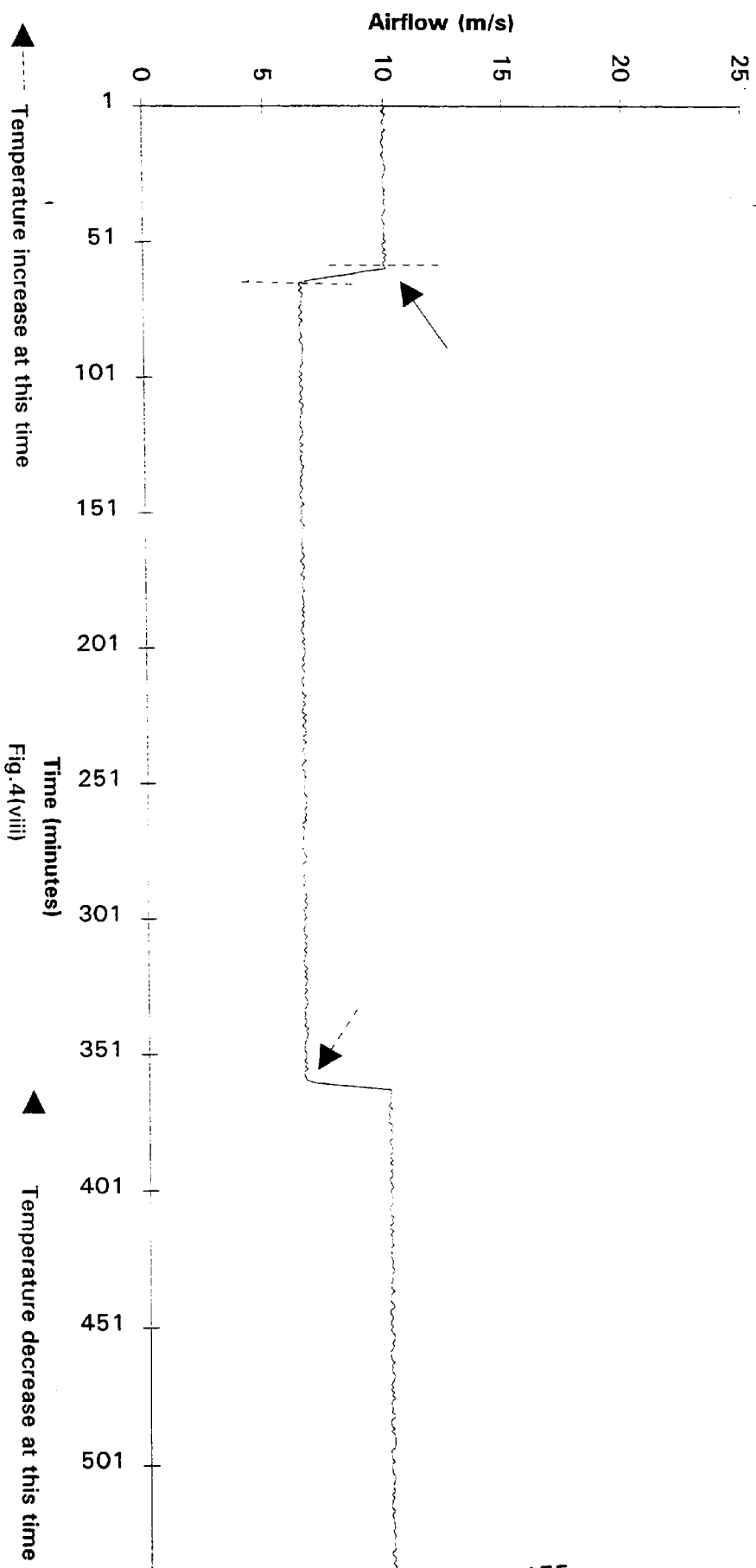
Analysis of Figure A(vii) revealed that the temperature of air drawn into the ball mill remained constant at 30°C (+/- 1°C) for the duration of the trial.

(iv) Airflow through the oxide mill

Figure 4(viii)

Analysis of the airflow profile represented in Figure 4(viii) revealed that prior to the increase in ball mill temperature the airflow was constant at its setpoint value of 10 m/s (+/- 0.1 m/s). However, five minutes after the increase in ball mill temperature the airflow through the process dropped to 6.5 m/s (+/- 0.1 m/s). The 15°C increase in temperature had resulted in a 3.5 m/s decrease in airflow. The airflow remained at 6.5 m/s for the five hour period.

**Figure 4(viii) Profile of the airflow through the oxide mill during the ball mill temperature steady state sensitivity trial**



Returning the ball mill temperature to 125°C resulted in the airflow increasing back to 10 m/s. The airflow reached 10 m/s, four minutes after the step change decrease in ball mill temperature. The airflow remained constant at 10 m/s for the remaining three hours of the trial.

Ideally, once the ball mill temperature had been changed, the setpoint conditions of each process variable should have been kept constant to determine the effect on the quality outputs. However the change which occurred in airflow was unavoidable. In practice it was too difficult to keep the airflow constant. Performing trials on industrial processes leads to complications which prevent total experimental control. The results of this trial appear to show that ball mill temperature changes affect lead oxide quality", in part any way," by producing small changes in airflow. During the airflow trial (4.7.1) no variations in ball mill temperature

were observed and hence the lead oxide quality variations in that trial were not the result of temperature fluctuations. It is therefore possible to disentangle the effects.

(b) Effect on lead oxide quality and rate of production

The time taken to increase the ball mill temperature from 125°C to 140°C was five minutes. The 15°C step change was achieved by turning off both water and fan cooling. The time required to return the ball mill temperature to 125°C was four minutes. This was achieved by having the water cooling facility continuously dumping water over the outside surface of the ball mill drum. Throughout the water cooling the fan was also continually on. The above time delays match the observed delay to airflow changes and thus a negligible delay between temperature and airflow can be deduced. The observed sensitivity is  $-0.23 \text{ m/s per } ^\circ\text{C}$ .

The effects on both lead oxide quality and rate of production over the ball mill temperature step change trial were:

(i) Free lead content

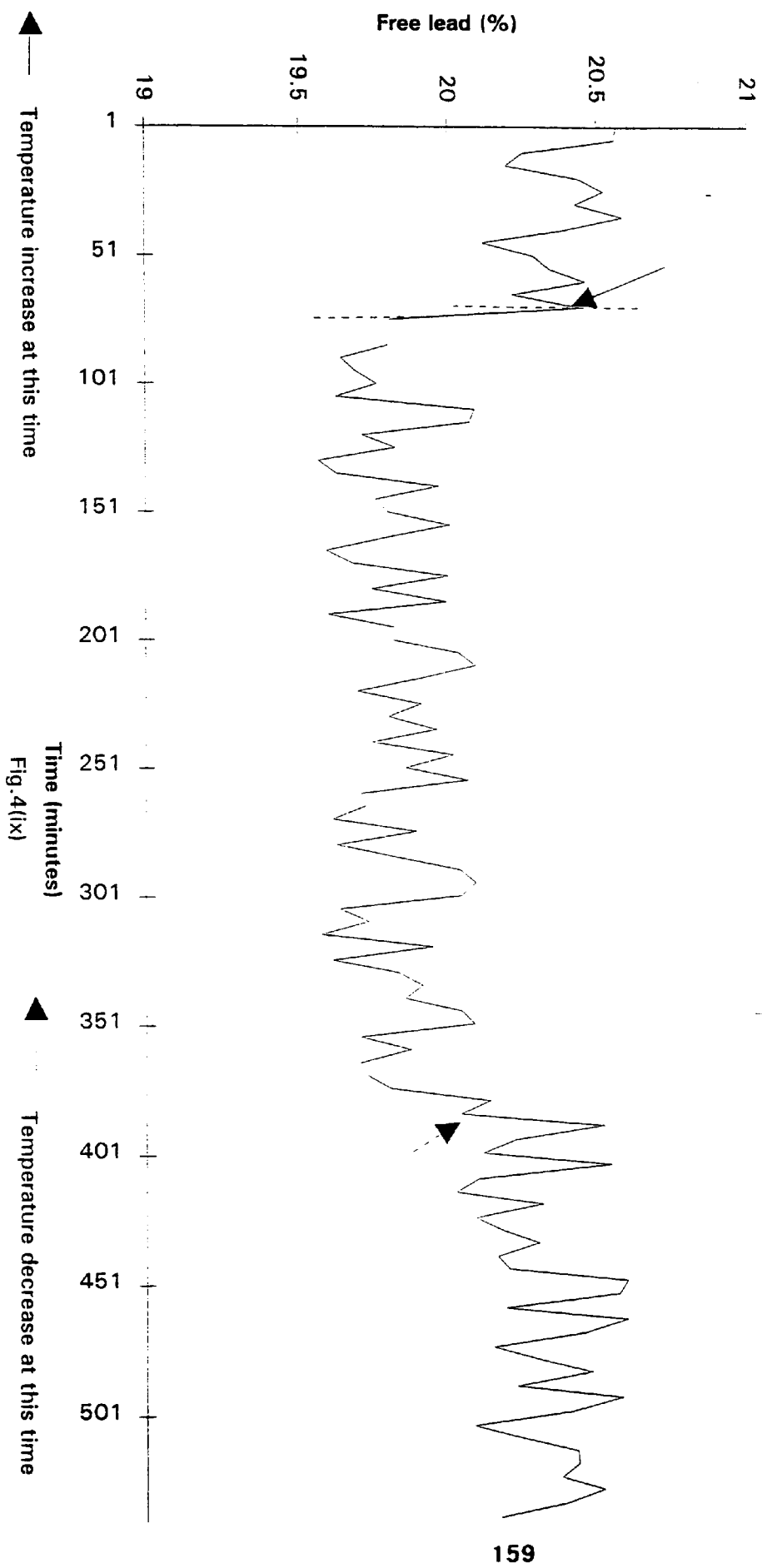
(Figure 4(ix))

The free lead prior to the steady state sensitivity trial was constant at 20.3% (  $\pm$  0.3%). Increasing the ball mill temperature from 125°C to 140°C resulted in the free lead decreasing to 19.8% (  $\pm$  0.3%). The free lead reached 19.8% (  $\pm$  0.3%), twenty minutes after the ball mill temperature was increased. The free lead remained constant at this range for the five hour period the ball mill temperature was at 140°C.

Returning the ball mill temperature to 125°C, resulted in free lead increasing back to 20.3% (  $\pm$  0.3%). The free lead reached this range nineteen minutes after decreasing the ball mill temperature. The free lead remained constant at 20.3% (  $\pm$  0.3%) for the remaining three hours of the trial.



**Figure 4 (ix) The effect of the ball mill temperature steady state sensitivity test on free lead**



The 15°C change in ball mill temperature resulted in the airflow decreasing from 10 m/s (+/- 0.1 m/s) to 6.5 m/s (+/- 0.1 m/s). Analysis of the airflow steady state sensitivity test (Section 4.7.1) revealed that the ball mill temperature remained constant. The change in free lead in that experiment was due to the 10 m/s variation in airflow. As no change in ball mill temperature was observed during the airflow test, all of the variations in that test (4.7.1) can be attributed to the airflow change and it is, therefore, possible to very simply separate the effects of the 3.5 m/s airflow change occurring in the current test from the direct effects of the change in ball mill temperature.

The airflow change of 3.5 m/s produced the 0.5% decrease in free lead content. If the effect of airflow on free lead was linear, a 3.5 m/s decrease should produce a 0.8% decrease in free lead content

because a 10 m/s increase in airflow produced a 2.4% change in free lead content (See page 141). However, the actual free lead decrease as a result of the ball mill temperature steady state sensitivity test was 0.5%, since a 0.8% decrease is due to the airflow change a 0.3% increase must be due to the direct effects of the temperature (That is, a sensitivity of 0.02% per °C).

The change in ball mill temperature which was used was the maximum temperature increase which the process could safely undergo and still only a very small variation in free lead content was observed. The results of the test proved that ball mill temperature had only a very small effect on free lead content and as such could not be used as the basis of an automated system for controlling the production of lead oxide.

Although the situation of two apparently independent input process

variables changing and producing a change in the free lead content occurred, to investigate the reason of how it occurred would be impractical. To find the reason would take a considerable number of additional steady state sensitivity tests, some way of maintaining the airflow at its setpoint value and many more measurements of free lead. This further work, although scientifically very interesting was not undertaken as the effect of large ball mill temperature variations on free lead content were so small and it was difficult to secure additional time on the process plant for the necessary experiments.

However, the times required to reach maximum responses in free lead after the change in ball mill temperature were longer than the times during the airflow steady state sensitivity. The reason for this was that during the ball mill temperature change, five minutes was required to increase the ball mill temperature and four

minutes was required to return it to the starting setpoint value. Hence more time was taken to change the airflow. As soon as the airflow reaches both 6.5 m/s and 10 m/s, the time required to produce the 0.5% change in free lead was again fifteen minutes. Thus the total time from the change in ball mill temperature to reaching the maximum response in free lead was twenty and nineteen minutes respectively.

(ii) Apparent density  
(Figure 4(x))

The apparent density property at the start of the trial was constant at  $1.28 \text{ g/cm}^3$  ( $\pm 0.01 \text{ g/cm}^3$ ). When the ball mill temperature was increased from  $125^\circ\text{C}$ , the apparent density increased to  $1.34 \text{ g/cm}^3$  ( $\pm 0.01 \text{ g/cm}^3$ ) twenty minutes after the step change increase. The apparent density remained constant at this value for the five hour period the ball mill temperature was at  $140^\circ\text{C}$ .

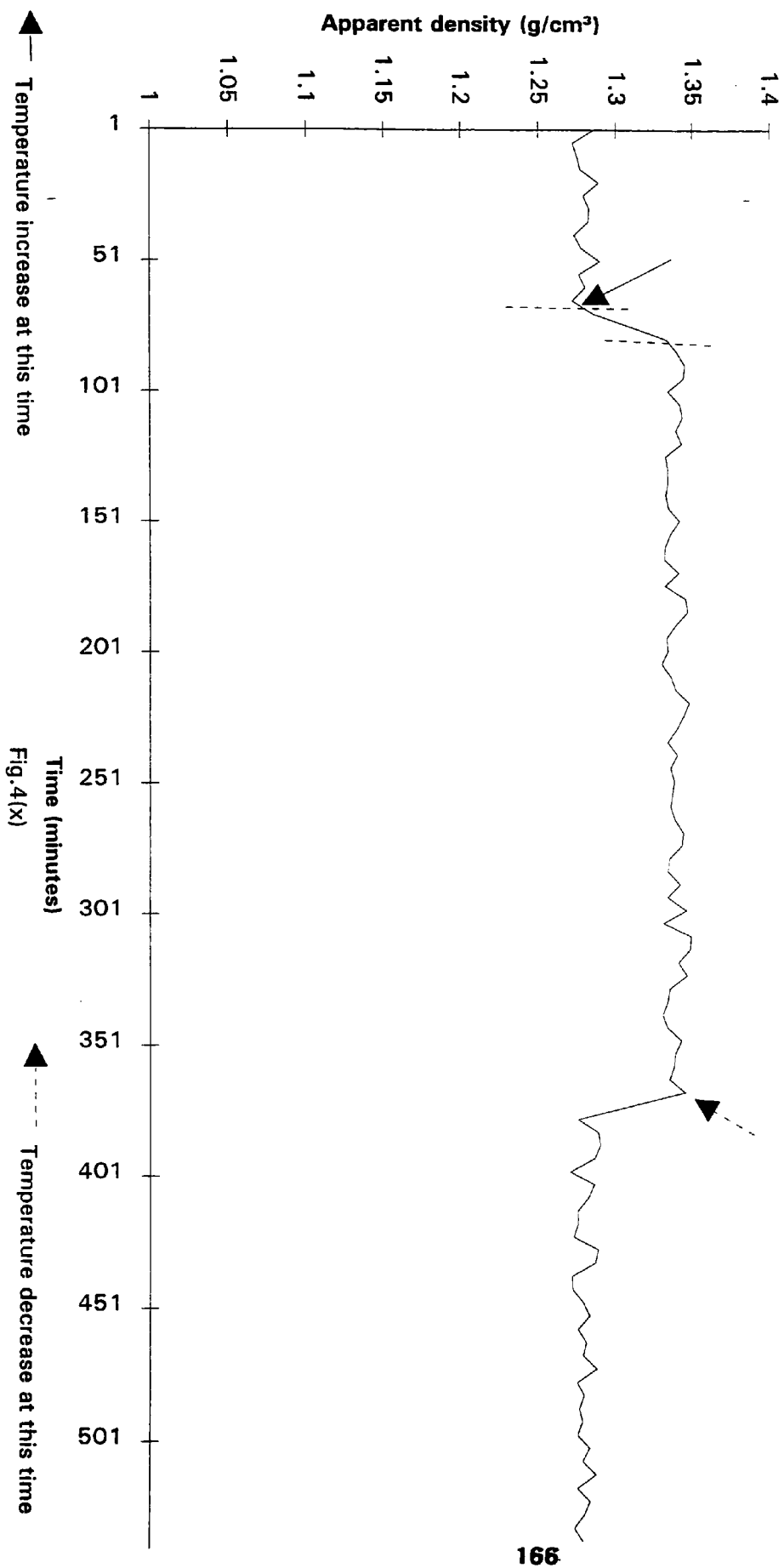
Returning the ball mill temperature to  $125^\circ\text{C}$ , resulted in the apparent density decreasing back to  $1.28 \text{ g/cm}^3$  ( $\pm 0.01 \text{ g/cm}^3$ ). This change occurred nineteen minutes after the decrease in ball mill temperature. The apparent density remained constant at  $1.28 \text{ g/cm}^3$  ( $\pm 0.01 \text{ g/cm}^3$ ) over the remaining three hours of the trial.

The airflow change of  $3.5 \text{ m/s}$  was the factor which produced most of the

0.06 g/cm<sup>3</sup> change in apparent density. The 3.5 m/s variation in airflow could be expected to produce a change of -0.067 g/cm<sup>3</sup> on its own. The observed change was only -0.06 g/cm<sup>3</sup>. Thus a change of +0.007 g/cm<sup>3</sup> was attributed to the 15°C temperature change directly. A sensitivity of 0.00047 g/cm<sup>3</sup> per °C.

Again the times required to produce the maximum response are different, due to the fact that it takes longer to increase and decrease the airflow via the ball mill temperature change.

**Figure 4(x) The effect of the ball mill temperature steady state sensitivity test on apparent density**





(iii) Rate of production of lead oxide  
(Figure 4(xi))

The lead oxide rate of production prior to the trial was 1.9 kg/min (+/- 0.1 kg/min). When the ball mill temperature was increased from 125 to 140°C, the production rate decreased to 1.34 kg/min (+/- 0.1 kg/min). The production reached 1.34 kg/min (+/- 0.1 kg/min) ten minutes after the ball mill temperature was changed. The rate of production remained constant at this value for the five hour period the ball mill temperature remained at 140°C.

Returning the ball mill temperature to 125°C, resulted in the rate of production increasing back to 1.9 kg/min (+/- 0.1 kg/min). The time taken to return the rate of production to 1.9 kg/min (+/- 0.1 kg/min) was nine minutes. The rate of production remained constant at this value over the remaining three hours of the trial.

**Figure 4(xi) The effect of the ball mill temperature steady state sensitivity test on lead oxide rate of production**

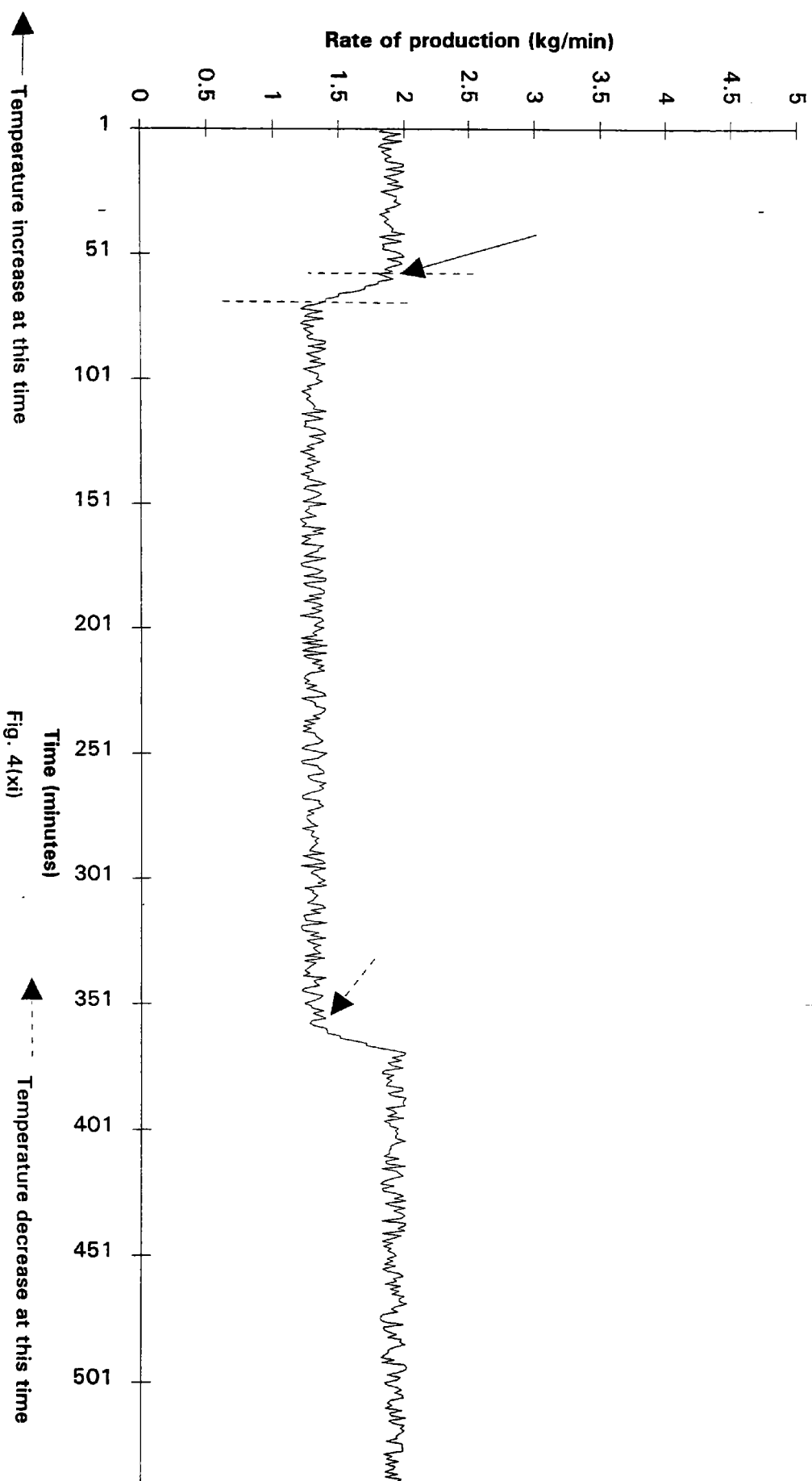


Fig. 4(xi)

The 3.5 m/s change in airflow would be expected to cause a change of - 0.56 kg/min. The observed change was 0.56 kg/min and so it may be concluded that all of the change was a result of the airflow disturbance and no change in production rate could be directly attributed to the change in mill temperature.

(C) COMPARISON OF THE FREE LEAD VARIATIONS (INDUCED BY THE BALL MILL TEMPERATURE STEADY STATE SENSITIVITY TEST) WITH THE PREVIOUSLY OBSERVED LEAD OXIDE QUALITY VARIATIONS DESCRIBED IN CHAPTER ONE

The variations in free lead content were:

- (i) At the start of the trial, the free lead content was 20.3% ( +/- 0.3%).
- (ii) During the five hour period after the change, the free lead was 19.8% (+/- 0.3%).
- (iii) Returning the ball mill temperature to the original setpoint value resulted in free lead returning back

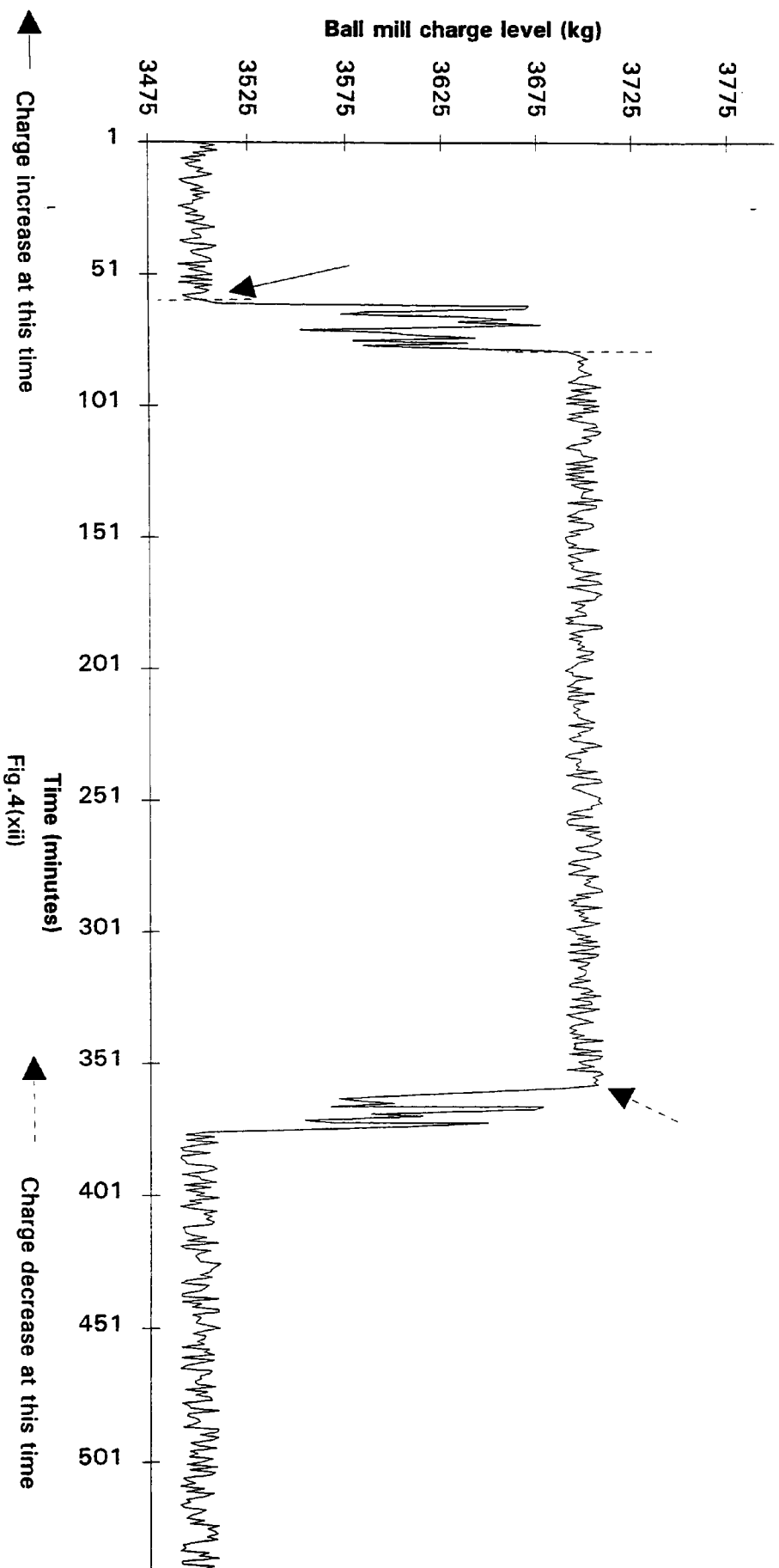
to 20.3% (+/- 0.3%).

These results clearly showed that throughout the ball mill temperature trial, the ranges in free lead values were not as great as the perviously observed variations of 19.3 to 27% in Chapter One (Figure 1(iii)). The 0.5% free lead variation induced by the ball mill temperature changes therefore revealed that the majority of the previously observed production variations in free lead were not caused by small uncontrolled variations in ball mill temperature, but could be attributed to the previously discussed measured errors.

#### 4.7.3 BALL MILL CHARGE LEVEL STEADY STATE SENSITIVITY TEST

The initial level of ball mill charge was set at 3,500 kg (+/- 10 kg). After one hour, the level was increased to 3,700 kg (+/- 10 kg). The charge level remained at that value for five hours, after which it was returned to its initial setpoint of 3,500 kg. The charge level was monitored at this value for a further three hours (Figure 4(xii)). Throughout the nine hour trial the lead oxide rate of production and the free lead and apparent density quality properties were continually monitored.

**Figure 4(xii) The profile of the ball mill charge level steady state sensitivity trial**



The other oxide mill process variables for the duration of the trial were kept constant. The ball mill temperature was 125°C, the relative humidity was 35%, the air temperature was 30°C and the airflow was 10 m/s.

#### 4.7.3.1 DISCUSSION OF THE BALL MILL CHARGE LEVEL STEADY STATE SENSITIVITY TEST

##### (a) Effect on the other process variables

For the duration of the charge level steady state sensitivity test, the other process variables were continually monitored.

##### (i) Ball mill temperature (Figure A(viii) Appendix)

The ball mill temperature was set at 125°C (+/- 1°C) prior to the start of the step change trial. Analysis of Figure A(viii) revealed that ball mill temperature remained constant at 125°C (+/- 1°C) over the trial period.

##### (ii) Relative humidity of air entering the ball mill (Figure A(ix) Appendix)

Figure A(ix) reveals that the relative humidity of air drawn into the ball mill had remained constant at 35% (+/- 2%) over the trial period.

(iii) Temperature of air entering the ball mill

(Figure A(x) Appendix)

Figure A(x) reveals that the temperature of air drawn into the ball mill had remained constant at 30°C (+/- 1°C) over the trial period.

(iv) Airflow through the oxide mill process

(Figure A(xi) Appendix)

Figure A(xi) reveals that the airflow remained constant at 10 m/s (+/- 0.1 m/s) over the trial period.

(b) Effect on lead oxide quality and rate of production

The time taken to both increase the level of charge to 3,700 kg and return it to 3,500 kg

was twenty minutes.

The effects on both lead oxide quality and rate of production over the charge level step change trial were:

(i) Free lead content

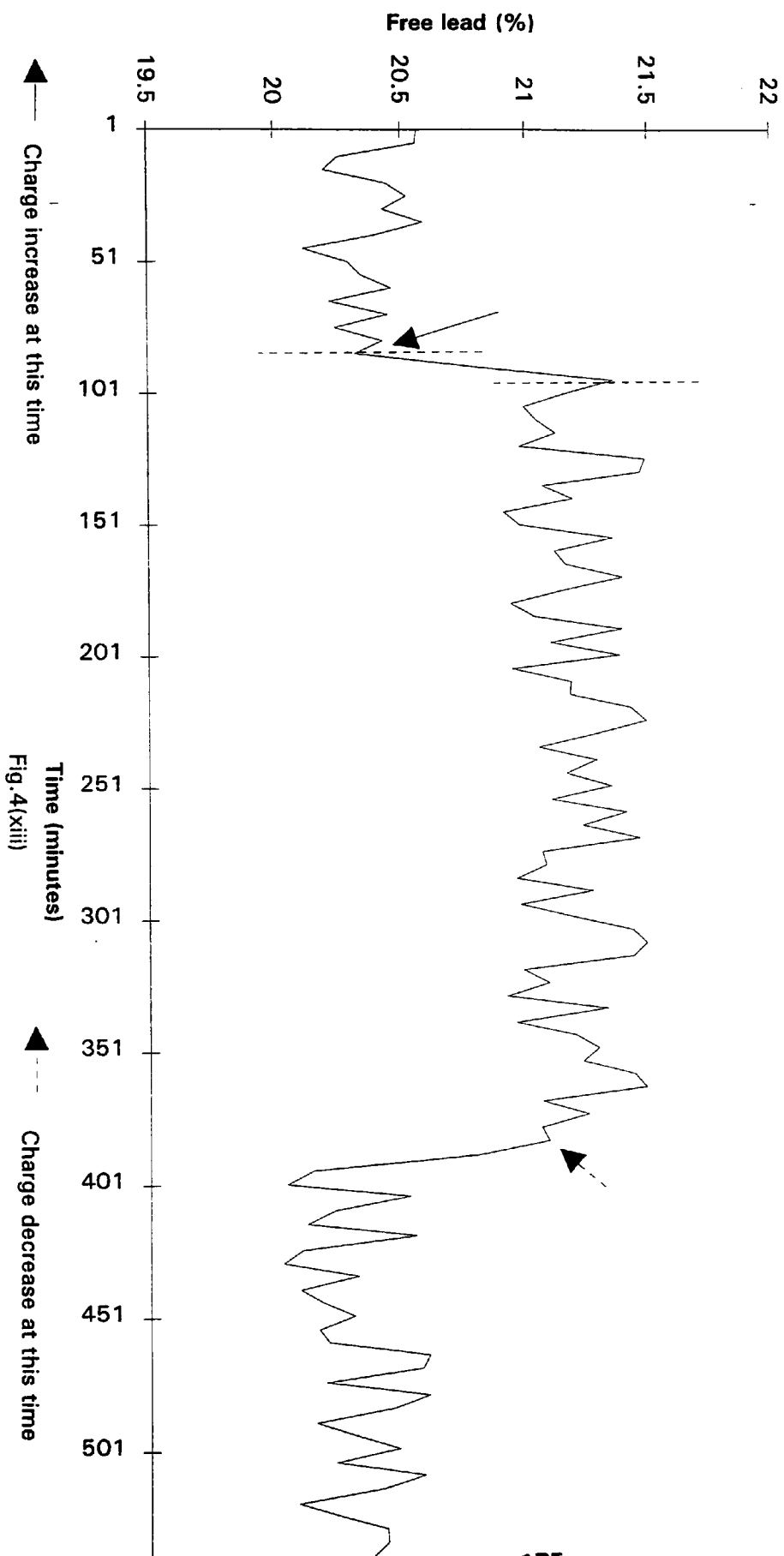
(Figure 4(xiii))

The free lead prior to the start of the trial was 20.3% (  $\pm$  0.3%). Increasing the level of charge from 3,500 kg to 3,700 kg resulted in free lead increasing to 21.2% (  $\pm$  0.3%). The free lead reached 21.2% (  $\pm$  0.3%) thirty-five minutes after the charge level was increased. The free lead remained at 21.2% (  $\pm$  0.3%) for the five hour period the charge level was at 3,700 kg.

Returning the level of charge to 3,500 kg, resulted in the free lead decreasing back to 20.3% (  $\pm$  0.3%). Again the free lead reached 20.3% (  $\pm$  0.3%), thirty-five minutes after decreasing the charge level. The free lead remained at 20.3% (  $\pm$  0.3%) for the remaining three hours of the trial.



**Figure 4(xiii) The effect of the ball mill charge level steady state sensitivity test on free lead**



Thus the sensitivity is 0.0045% per kilogram with a delay of thirty five minutes. The tumbling action of lead pellets in the ball mill produce small abrasions of lead which oxidise in the airstream which flows through the ball mill. Significantly increasing the charge level of lead pellets in the ball mill resulted in the freshly produced lead oxide powder being removed at a faster rate from the ball mill. At the high charge level, the horizontal stream of air flows directly through the main bulk of lead oxide powder in the ball mill. As a result, the powder can be easily removed and the faster removal of lead oxide powder resulted in less oxidation. Therefore, lead oxide powder produced at the high charge level of 3,700 kg had an increased content of free-lead.

(ii) Apparent density property

(Figure 4(xiv))

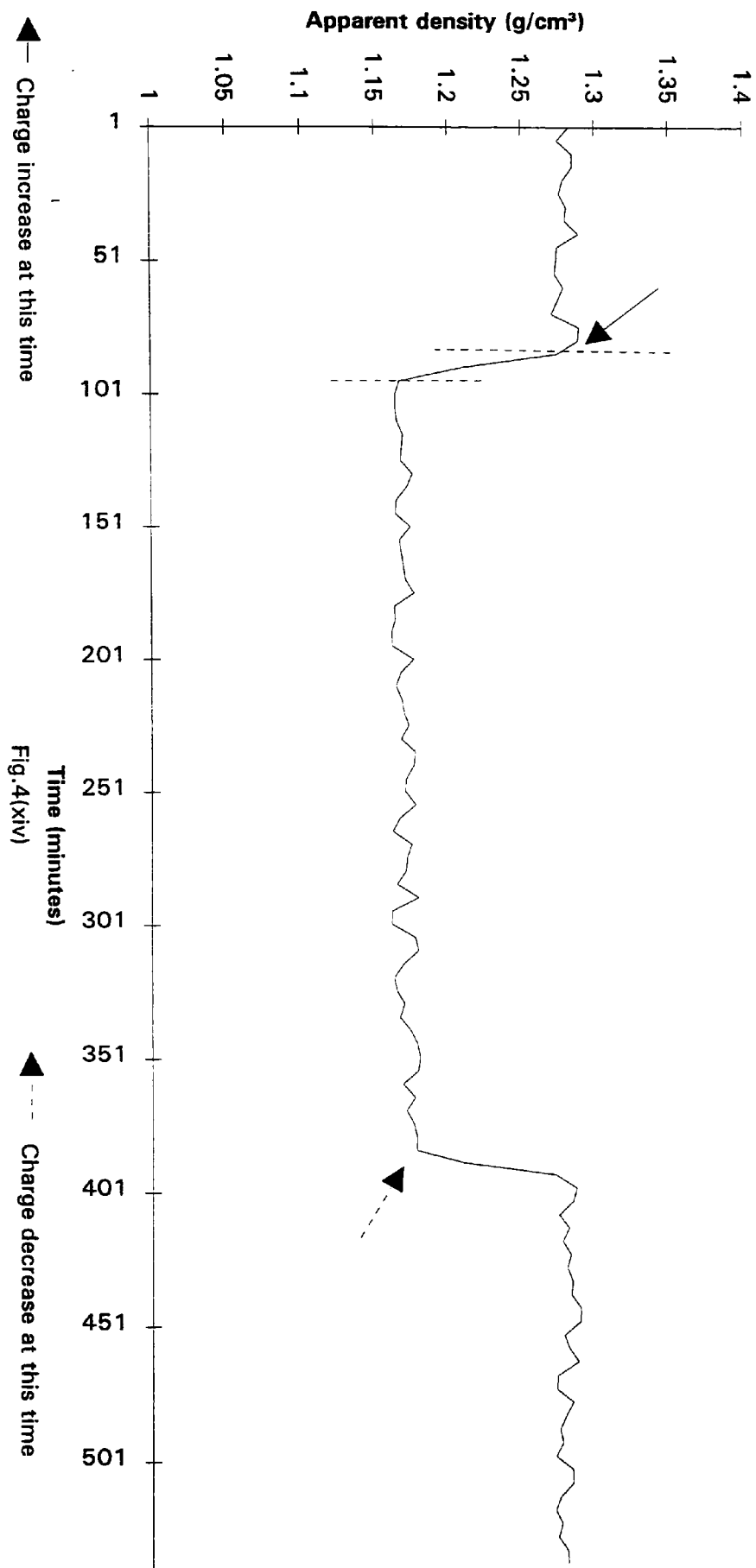
The apparent density prior to the start of the trial was constant at  $1.28 \text{ g/cm}^3$  ( $\pm 0.01 \text{ g/cm}^3$ ). When the ball mill charge level was increased to 3,700 kg, the

apparent density of the freshly produced lead oxide powder dropped to  $1.18 \text{ g/cm}^3$  ( $\pm 0.01 \text{ g/cm}^3$ ). The apparent density reached  $1.18 \text{ g/cm}^3$  ( $\pm 0.01 \text{ g/cm}^3$ ) thirty-five minutes after the charge level was changed. The apparent density remained constant at this value for the five hour period the charge level was 3,700 kg.

Returning the charge level to 3,500 kg resulted in the apparent density increasing back to  $1.28 \text{ g/cm}^3$  ( $\pm 0.01 \text{ g/cm}^3$ ). Again the time taken was thirty-five minutes. The apparent density remained constant at  $1.28 \text{ g/cm}^3$  ( $\pm 0.01 \text{ g/cm}^3$ ) over the remaining three hours of the trial. Thus the sensitivity is  $-0.0005 \text{ g/cm}^3$  per kilogram with a delay of thirty five minutes.

The charge level of 3,700 kg enables lead oxide powder to be removed very easily from the ball mill. As a result, large particles of lead oxide powder can also be easily removed from the ball mill. The larger particles find it difficult to pack together and as a result the samples had low apparent density values.

**Figure 4(xiv) The effect of the ball mill charge level steady state sensitivity test on apparent density**



Time (minutes)

Fig. 4(xiv)

(iii) Rate of production of lead oxide  
(Figure 4(xv))

The lead oxide rate of production prior to the trial was constant at 1.9 kg/min ( $\pm$  0.1 kg/min). When the level of charge was increased from 3,500 kg to 3,700 kg the production rate increased to 4.10 kg/min ( $\pm$  0.1 kg/min). The production rate reached 4.10 kg/min ( $\pm$  0.1 kg/min) twenty minutes after the ball mill charge level was changed. The rate of production remained constant at 4.10 kg/min ( $\pm$  0.1 kg/min) for the five hour period the charge level was at 3,700 kg. Running the oxide mill at 3,700 kg resulted in the lead oxide production rate more than doubling from 1.9 to 4.10 kg/min. The company are now reluctant to run the oxide mills at low charge-levels.

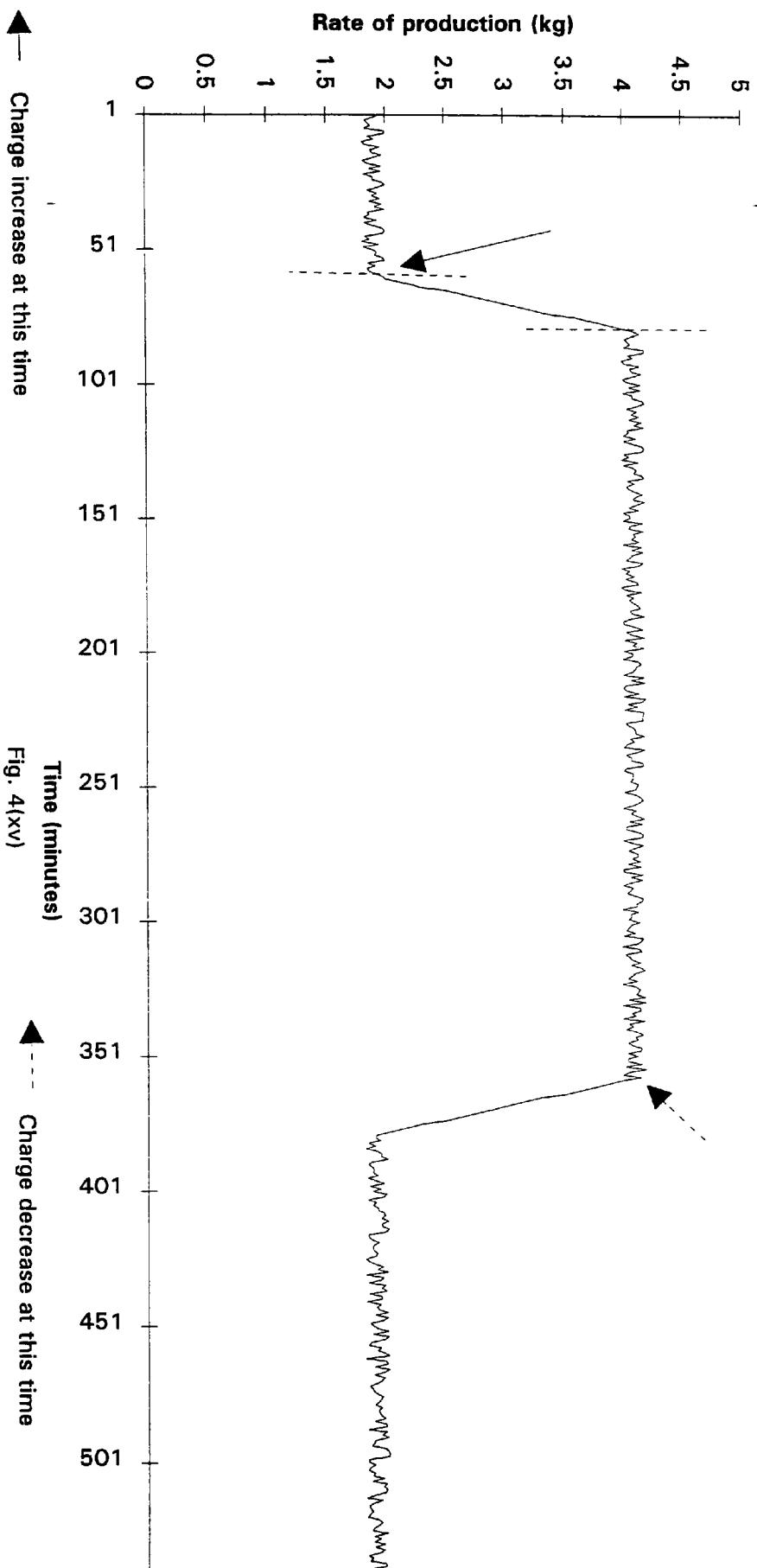
Returning the charge level to 3,500 kg, resulted in the rate of production decreasing back to 1.9 kg/min. Again the time taken was twenty minutes. The rate of production remained constant at 1.9 kg/min ( $\pm$  0.1 kg/min) over the remaining three hours of the trial. Thus the

sensitivity of production rate is 0.011 kg/min per kilogram with a delay of twenty minutes.

At the lower charge level of 3,500 kg, the main bulk of lead oxide powder escapes the horizontal airflow stream through the ball mill. As a result, the freshly produced lead oxide powder cannot be easily removed. Therefore a low rate of production occurs.

However, at the high charge level of 3,700 kg, the horizontal stream of air flows directly through the main bulk of lead oxide powder in the ball mill. As a result, the powder can be easily removed and therefore causes the rate of production to increase.

**Figure 4(xv) The effect of the ball mill charge level steady state sensitivity test on lead oxide rate of production**



(C) COMPARISON OF THE FREE LEAD VARIATIONS (INDUCED BY THE CHARGE LEVEL STEADY STATE SENSITIVITY TEST) WITH THE PREVIOUSLY OBSERVED LEAD OXIDE QUALITY VARIATIONS DESCRIBED IN CHAPTER ONE

The variations in free lead during the trial were:

- (i) At the start of the trial, the free lead was 20.3% (+/- 0.3%).
- (ii) During the five hour period after the change , the free lead content was 21.2% (+/- 0.3%).
- (iii) Returning the charge level to its original setpoint resulted in free lead returning back to its starting value of 20.3% (+/- 0.3%).

These results revealed that the 0.9% variation in free lead was not as great as the previously observed variations of 19.3 to 27% in Chapter One (Figure 1(iii)). The charge level steady state sensitivity trial therefore revealed that uncontrollable variations in the level of ball mill charge were not solely responsible for the previously observed quality variations in



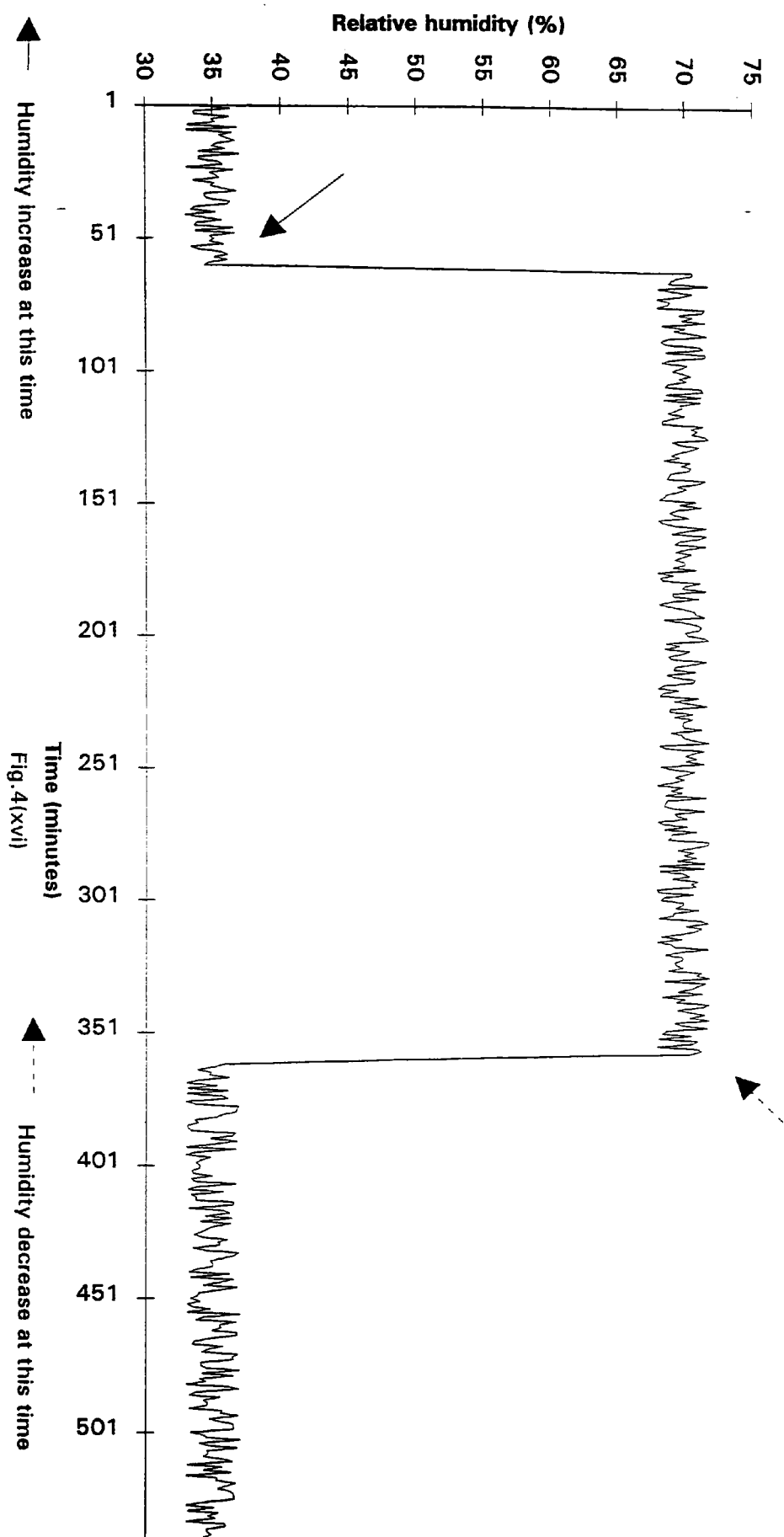
freshly produced lead oxide powder.

#### 4.7.4 Relative humidity steady state sensitivity test

The percentage relative humidity in the area directly in front of the ball mill was set at 35% (+/- 2%). After one hour, the relative humidity was increased to 70% (+/- 2%). The relative humidity remained at this value for five hours, after which it was returned to its initial setpoint of 35% (+/- 2%). The relative humidity was monitored at this setpoint for a further three hours (Figure 4(xvi)). Throughout the nine hour trial, the lead oxide rate of production and the free lead and apparent density quality properties were continually monitored.

The other oxide mill process variables for the duration of the trial were kept constant. The ball mill temperature was 125°C, the ball mill charge level was 3,500 kg, the air temperature was 30°C and the airflow was 10 m/s.

**Figure 4(xvii) Profile of the relative humidity steady state sensitivity trial**



#### 4.7.4.1 DISCUSSION OF THE RELATIVE HUMIDITY STEADY STATE SENSITIVITY TEST

##### (a) Effect on the other process variables

For the duration of the relative humidity step change trial, the other process variables were continually monitored.

##### (i) Ball mill temperature

(Figure A(xii) Appendix)

The setpoint for the ball mill temperature was 125°C (+/- 1°C). Analysis of Figure A(xii) revealed that the ball mill temperature had remained constant at 125°C (+/- 1°C) over the trial period.

##### (ii) Level of ball mill charge

(Figure A(xiii) Appendix)

At the start of the trial, the charge level was set at 3,500 kg (+/- 10 Kg). Analysis of Figure A(xiii) revealed that the charge level had remained constant over the trial period.

(iii) Temperature of air entering the ball mill

(Figure A(xiv) Appendix)

Figure A(xiv) reveals that the temperature of air drawn into the ball mill remained constant at 30°C (+/- 1°C) over the trial period.

(iv) Airflow through the oxide mill

(Figure A(xv) Appendix)

Figure A(xv) reveals that the airflow remained constant at 10 m/s (+/- 0.1 m/s) over the trial period.

(b) Effect on lead oxide quality and rate of production

The time taken to both increase the relative humidity to 70% and return it back to 35% was two minutes. This was achieved by using different steam flow rates in the area directly in front of the ball mill.

The effects on both lead oxide quality and rate of production during the relative humidity steady state sensitivity trial were:

(i) Free lead content

(Figure A(xvi) Appendix)

The free lead prior to the trial was 20.3% (+/- 0.3%). Increasing the relative humidity from 35% to 70% had no effect on free lead. For the five hour period the relative humidity was at 70% (+/- 2%) no variation in the free lead occurred. Also returning the relative humidity to 35% (+/- 2%) produced no change in the free lead property.

(ii) Apparent density

(Figure A(xvii) Appendix)

The apparent density prior to the trial was constant at 1.28 g/cm<sup>3</sup> (+/- 0.1 g/cm<sup>3</sup>). Increasing the relative humidity from 35% to 70% had no effect on the apparent density property. For the five hour period, the relative humidity was at 70% (+/- 2%), the apparent density remained constant at 1.28 g/cm<sup>3</sup> (+/- 0.01 g/cm<sup>3</sup>). Also returning the relative humidity to 35% (+/- 2%) produced no

change in apparent density.

- (iii) Rate of production of lead oxide  
(Figure A(xviii) Appendix)

The lead oxide rate of production prior to the trial was 1.9 kg/min (+/- 0.1 kg/min). Increasing the relative humidity from 35% to 70% had no effect on the rate of production. Also returning the relative humidity to 35% (+/- 2%) produced no change in production rate.

- (C) COMPARISON OF THE FREE LEAD VARIATIONS (INDUCED BY THE RELATIVE HUMIDITY STEADY STATE SENSITIVITY TEST) WITH THE PREVIOUSLY OBSERVED LEAD OXIDE QUALITY VARIATIONS DESCRIBED IN CHAPTER ONE

No variations in the free lead property were observed during the relative humidity trial. For the duration of the nine hour test, the free lead content remained constant at 20.3% (+/- 0.3%). The results of this trial therefore revealed that the previously observed variations in free lead were not caused by fluctuations in the relative humidity of air

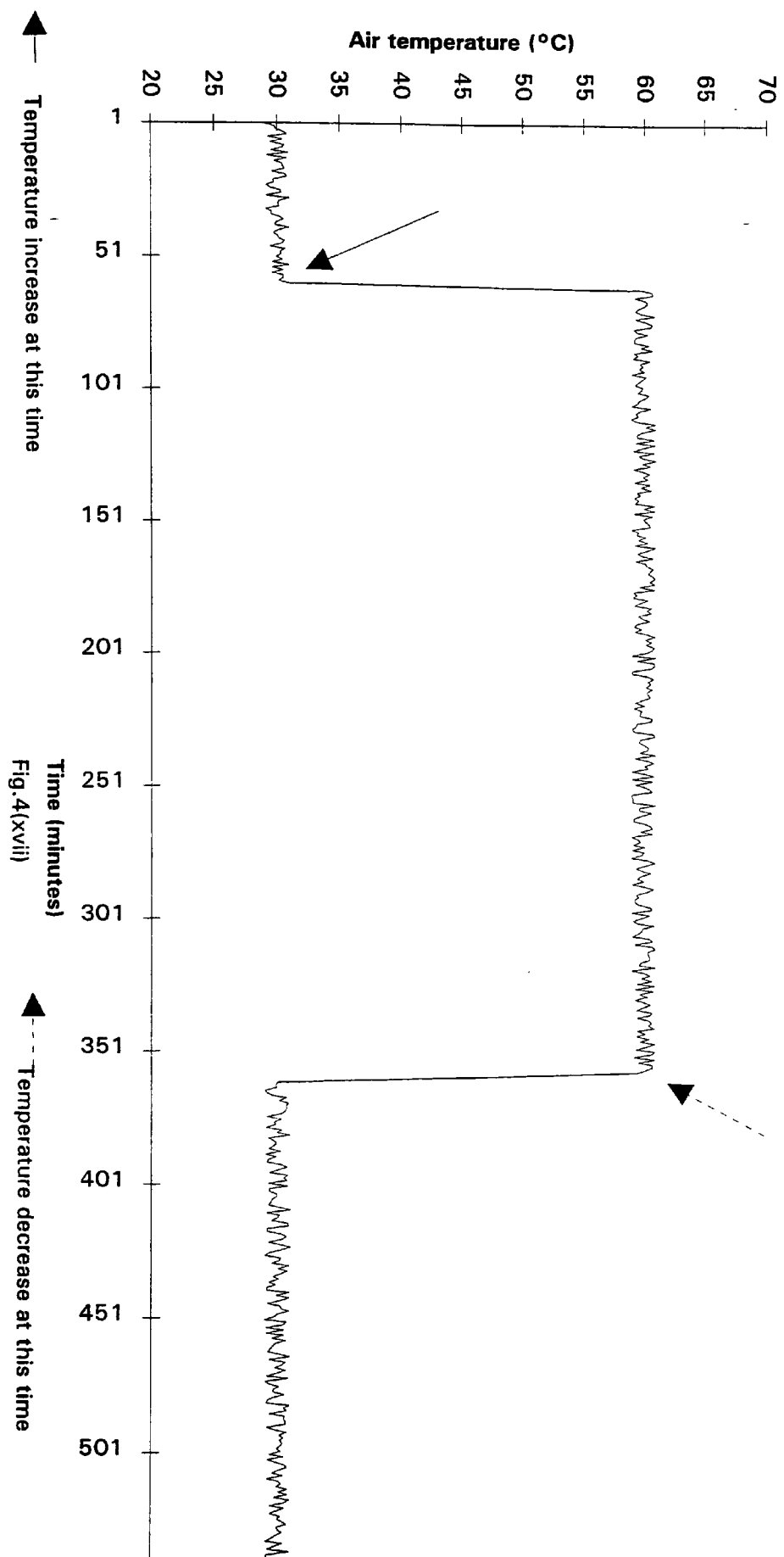
being drawn into the ball mill.

#### 4.7.5 AIR TEMPERATURE STEADY STATE SENSITIVITY TEST

The air temperature in the area directly in front of the ball mill was set at 30°C (+/- 1°C). After one hour, the air temperature was increased to 60°C (+/- 1°C). The air temperature remained at this setpoint for five hours, after which it was returned to its initial value of 30°C. The air temperature was monitored at this setpoint for a further three hours (Figure 4(xvii)). Throughout the nine hour trial, the lead oxide rate of production and the free lead and apparent density quality properties were continually monitored.

The other oxide mill process variables for the duration of the trial were kept constant. The ball mill temperature was 125°C, the ball mill charge level was 3,500 kg, the airflow was 10 m/s and the relative humidity was 35%.

**Figure 4(xvii) Profile of the air temperature steady state sensitivity trial**





#### 4.7.5.1 DISCUSSION ON THE AIR TEMPERATURE STEADY STATE SENSITIVITY TEST

##### (A) Effect on the other process variables

For the duration of the air temperature step change trial, the other process variables were continually monitored.

###### (i) Ball mill temperature

(Figure A(xix) Appendix)

Figure A(xix) reveals that the ball mill temperature had remained constant at 125°C (+/- 1°C) over the trial period.

###### (ii) Level of ball mill charge

(Figure A(xx) Appendix)

Figure A(xx) reveals that the mill charge remained constant at 3500 kg (+/- 10 kg) over the trial period.

###### (iii) Airflow through the oxide mill

(Figure A(xxi) Appendix)

Figure A(xxi) reveals that the airflow remained constant at 10 m/s

( $\pm$  0.1 m/s) over the trial period.

(iv) Relative humidity of air entering the ball mill

(Figure A(xxii) Appendix)

Figure A(xxii) reveals that the relative humidity of air drawn into the ball mill had remained constant at 35% ( $\pm$  2%) over the trial period.

(B) EFFECT ON LEAD OXIDE QUALITY AND RATE OF PRODUCTION

The time taken to both increase the air temperature to 60°C and return it to 30°C was two minutes. The temperature changes were achieved by using an industrial butane gas heater in the area directly in front of the ball mill.

The effects on both lead oxide quality and rate of production during the relative humidity trial were:

(i) Free lead content

(Figure A(xxiii) Appendix)

The range in free lead prior to the trial was constant at 20.3% ( $\pm 0.3\%$ ). Increasing the air temperature from 30°C to 60°C had no effect on free lead. For the five hour period, the air temperature was at 60°C ( $\pm 1^\circ\text{C}$ ) no variation in free lead occurred. Also returning the air temperature to 30°C ( $\pm 1^\circ\text{C}$ ) produced no change in the free lead property.

(ii) Apparent density

(Figure A(xxiv) Appendix)

The apparent density prior to the trial was constant at 1.28 g/cm<sup>3</sup> ( $\pm 0.01$  g/cm<sup>3</sup>). Increasing the air temperature from 30°C to 60°C had no effect on apparent density. For the five hour period, the air temperature was at 60°C ( $\pm 1^\circ\text{C}$ ), the apparent density remained constant at 1.28 g/cm<sup>3</sup> ( $\pm 0.01$  g/cm<sup>3</sup>). Also returning the air temperature to 30°C ( $\pm 1^\circ\text{C}$ ) produced no change in the apparent density property.

(iii) Rate of production of lead oxide  
(Figure A(xxv) Appendix)

The lead oxide rate of production prior to the trial was 1.9 kg/min (+/- 0.1 kg/min). Increasing the air temperature from 30°C to 60°C had no effect on production rate. Also returning the air temperature to 30°C (+/- 1°C) produced no change in production rate.

(C) COMPARISON OF THE FREE LEAD VARIATIONS (INDUCED BY THE AIR TEMPERATURE STEADY STATE SENSITIVITY TEST) WITH THE PREVIOUSLY OBSERVED LEAD OXIDE QUALITY VARIATIONS DESCRIBED IN CHAPTER ONE

No variations in the free lead property were observed during the air temperature trial. For the duration of the nine hour test, the free lead content remained at 20.3% (+/- 0.3%). The results of this trial, therefore revealed that the previously observed variations in free lead were not caused by fluctuations in the temperature of air being drawn into the ball mill.

Analysis of steady state sensitivity results clearly shows that the previously observed variations of lead oxide quality in Chapter One were not caused by the process variables fluctuating from their setpoint conditions. During the trials, the continuous monitoring of the process variables airflow, ball mill temperature and ball mill charge level revealed that they were always constant at their setpoint value. Hence the methods used to control the process variables were considered very reliable and could therefore be depended upon to keep the process variables constant at their setpoint conditions.

The effect of each process variable change on lead oxide quality and rate of production revealed that:

- (i) Both the air temperature and relative humidity step changes had no effect on either lead oxide quality nor the production rate. Hence the hypotheses which proposed that quality variations could have been caused by fluctuations in the climatic conditions (the temperature and relative humidity of the air drawn into the ball mill) were dismissed. It appears that the quality of freshly

produced ball mill lead oxide was totally independent of the climatic conditions in the area directly in front of the ball mill.

- (ii) The 10 m/s airflow change resulted in a 2.4% variation in free lead content, a 0.19 g/cm<sup>3</sup> variation in apparent density and a 1.6 kg/min increase in the rate of production. The sensitivity was 0.24% per m/s with a delay of fifteen minutes, - 0.0019 g/cm<sup>3</sup> per m/s with a delay of fifteen minutes and 0.16 kg/min per m/s with a delay of five minutes.
  
- (iii) The ball mill temperature steady state sensitivity test resulted in a 0.5% variation in free lead content, a 0.06 g/cm<sup>3</sup> variation in apparent density and a 0.56 kg/min variation in the rate of production. The ball mill temperature change of 15°C clearly induced a 3.5 m/s change in the airflow through the process. This airflow change induces variations as in (ii) in addition the temperature directly affects percentage free lead with a sensitivity of 0.02% per °C and the apparent density with a sensitivity of

0.0047 g/cm<sup>3</sup> per °C.

- (iv) The charge level change of 200 kg resulted in a 0.9% variation in free lead, a 0.10 g/cm<sup>3</sup> variation in apparent density and a 2.2 kg/min increase in the rate of production. The sensitivity being 0.0045% per kilogram for free lead, -0.005 g/cm<sup>3</sup> per kilogram for apparent density and 0.011 kg/min per kilogram for production rate.

The steady state sensitivity trials provided valuable information for developing a system for automatically controlling the oxide mill process to enable consistent lead oxide powder to be produced at a high rate of production. A block diagram of the plant is shown in Figure 4(xviii).

Figure 4(xviii) Block diagram of the plant

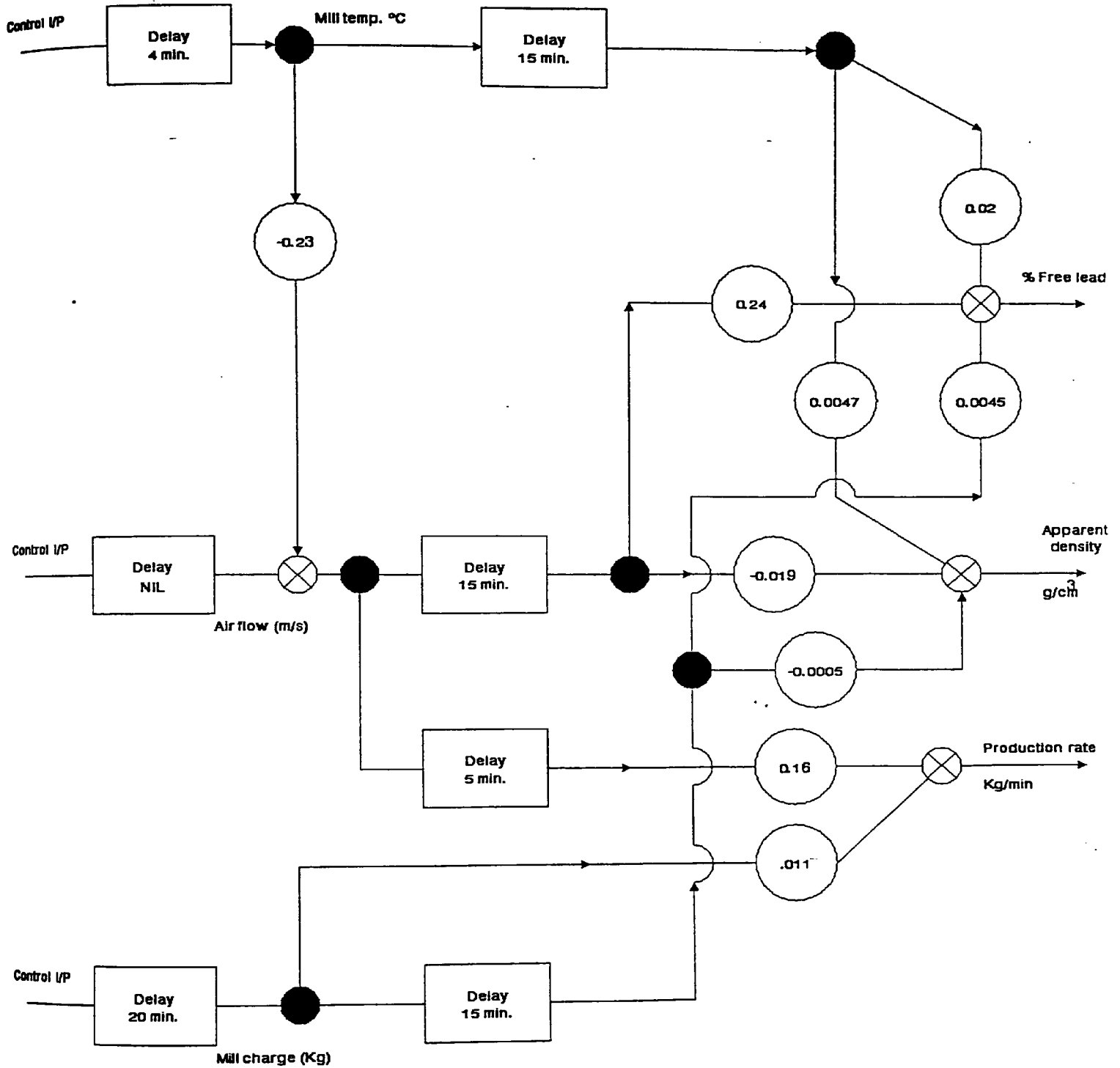


Figure 4(xviii)



The results of the ball mill temperature change revealed that the maximum temperature change only produced a small variation in lead oxide quality and rate of production. Therefore the ball mill temperature process variable was not considered as being the basis for the control strategy.

The control strategy for the automated control system will be based on the airflow, whilst the ball mill charge level will also be kept constant at a setpoint value. The airflow steady state sensitivity test revealed it had the greatest effect on quality whereas the charge level steady state sensitivity test revealed it had the greatest effect on rate of production.

Hence the airflow will be used to control quality and the rate of production will be fixed at a high rate by running the ball mill at a constant high level of charge. Using a charge level of 3,700 kg will ensure a minimum production rate of 4.11 kg/min at low airflow. On using higher airflows, higher rates of lead oxide rate of production will hopefully be achieved.

The control strategy will vary the airflow according to which values of free lead and apparent density

values are obtained. For example, if free lead content is too low, the control strategy will increase the airflow, if the free lead content is too high, the control strategy will decrease the airflow.

Depending on what type of lead oxide quality produces a paste density of 4.10 g/cm<sup>3</sup>, the control system will be set up to ensure that the oxide mill process only produces a particular type of lead oxide quality.

#### 4.9 THE PROPOSED CONTROL SYSTEM

##### INTRODUCTION

The manual system used by the operator involves collecting a lead oxide sample and manually assessing the quality off-line. If the results fall within the recommended specification range the operators do not alter the process variables. However, if the results of the quality tests have approached either the lower or upper specification limits; the operators manually adjust one of the process variables from its setpoint value in an attempt to return quality to the middle of the specification range.

The proposed control system will also rely upon the operators performing an off-line quality test.

However, instead of having the operators decide if the results are satisfactory, the control strategy will perform this function. As soon as the operators have finished both quality tests, the results will be typed via a computer into a control strategy program. The entered quality results will be compared with stored data. For example, the control strategy will have the free lead and apparent density values over the airflow range of 10 to 20 m/s at a ball mill temperature of 125°C and a ball mill charge level of 3,700 kg (Table 4(i) represents the type of data which will be in the control strategy).

Table 4(i)      Lead oxide quality comparison table for use in the airflow process variable control strategy

Airflow (m/s)	Free lead (%)	Apparent density (g/cm <sup>3</sup> )
10	21.5	1.17
13.5	22.5	
17	23.5	
20	24.5	
		0.98

Table 4(i)

The ball mill temperature and level of ball mill charge will be continually monitored to ensure that both remain constant at their setpoint conditions.

If alterations in the quality of produced lead oxide occur, the control strategy will instruct a programmable logic controller (PLC) to change the

fan speed.

Also the system should keep a tight check on the accuracy of the operator quality results. The control system should not accept a quality result which did not compare to a stored quality value at the particular airflow range.

The automated control system will also continually monitor the mechanical features of the oxide mill which have had a history of premature failure. The essential monitoring will help with preventative maintenance and as a result will hopefully reduce the oxide mill down time to a minimum.

#### 4.10 OVERALL CONCLUSION FOR CHAPTERS ONE TO FOUR

Having investigated both explanations, it appears that experimental error whilst performing the free lead titration was the main cause of the previously observed variations in free lead. The inaccurate results were then used by the operators to manually control the ball mill process. However, as the results were inaccurate, the operators adjusted process variables unnecessarily which resulted in further quality variations. Hence the effect of both these factors helped produce considerable daily variations in free lead content.

With the introduction of the new experimental procedure for measuring free lead, and the reintroduction of the apparent density test, it is hoped that experimental errors will be minimised whilst measuring lead oxide quality. Together with the introduction of accurate tests, the development of an automated control system will remove the responsibility for controlling the oxide mill process from the operators. Hence the new quality tests and control system will together ensure that the ball mill process will produce consistent quality lead oxide powder.

As a result of solving the problems of lead oxide quality variations, the type of lead oxide quality which produced a positive paste density of  $4.10 \text{ g/cm}^3$  can be found. As soon as the appropriate lead oxide quality is determined, the control strategy can be set up to produce only lead oxide powder of that quality. The control concepts have been adopted by the company and the control system is currently up and running on the oxide mills. The automated system has shown itself to be a vast improvement on the manually controlled process by enabling both consistent quality and high production rates to be achieved. Unfortunately due to company confidentiality present production records are unable to be shown.

## CHAPTER FIVE

### 5.0      THE EFFECT OF LEAD OXIDE QUALITY ON PASTE COMPOSITION<sup>6,10,11,12</sup>

Battery paste (The "active material") is the chemical basis of battery electrodes. It provides the active material with sufficient porosity, rigidity and cohesion to withstand vibration in service as well as the dimensional changes that occur during charging and discharging over the specified lifetime of a battery. Battery paste is the major variable which influences the capacity and lifetime of sealed lead acid batteries.

The production of battery paste involves the addition and mixing of lead oxide powder, 1.4 SG sulphuric acid, water and polypropylene fibres in large on-line mixers. The company has two on-line mixers which are capable of producing 1,000 kg batches of paste. Both are run continuously to keep pace with production demands. The composition of each paste batch is determined by performing an off-line density test. The test involves uniformly packing a cup of known volume with paste and weighing it. The volume and weight of paste is known, therefore the density can be calculated.

Having improved both the method of controlling the quality of freshly produced lead oxide powder and the test used to measure the percentage of free lead, tests to establish the effect of lead oxide powder on the density of freshly mixed pastes could begin. Lead oxide powder is the main ingredient of pastes and its fluctuations in quality are thought to be responsible for the previously observed fluctuations in paste density shown in Chapter One, Figure 1(i). These results revealed that paste density values varied from bottom ( $4.0 \text{ g/cm}^3$ ) to top specification ( $4.18 \text{ g/cm}^3$ ) over a week's production. It was hypothesised that variations of this magnitude could have serious consequences on battery lifetime and performance. Therefore, the aim of the project was to ensure that battery paste be routinely produced with consistent composition to eliminate variations in battery lifetime and performance.

A paste density of  $4.10 \text{ g/cm}^3$  was the target composition. The company believe that batteries which contained positive electrodes made with this positive paste density have excellent performance and lifetime properties. As variations in lead oxide quality are considered to be responsible for the fluctuations in paste density, it can be assumed that a specific specification of lead oxide powder is required to produce batches of paste with a density

of 4.10 g/cm<sup>3</sup>. The investigation of this hypothesis involved performing a series of tests whereby a number of different samples of lead oxide powder were mixed into trial batches of paste, to determine which particular specification was needed to produce a paste density of 4.10 g/cm<sup>3</sup>.

The composition of each trial batch of paste was also assessed by performing a stiffness test. Paste stiffness is defined as the resistance of paste to increasing force and it was hypothesised, from observations made by experienced plant operatives, that variations in the stiffness of freshly mixed pastes could lead to problems during pasting. At pasting, a rotating twin-bladed propeller contained in the pasting hopper forces paste into cast lead alloy grids. The blades are automatically controlled and the grid feeding rate is set, hence the only variable parameter is paste stiffness. Paste is applied onto grids with constant force, but if paste stiffness varies, problems could occur in the transfer of paste onto the grids. For example, the quantity (or thickness) of paste added might vary, or the paste might not adhere properly to the grids.

The measurement of both density and stiffness values for each trial batch of paste, allowed the stiffness to be known at the ideal paste density of 4.10 g/cm<sup>3</sup>.



If paste stiffness appears to the operators to be too low at this density, a compromise can be reached. To be able to measure paste stiffness, a test was designed which allowed a paste sample to be subjected to a range of forces in order to determine paste flow properties (see Section 5.3). The test was not intended to be introduced as a new off-line test for assessing composition. It was only used for the duration of the trial to ensure that an acceptable stiffness was reached at the required paste density of 4.10 g/cm<sup>3</sup>.

The production demands imposed on the company's two large paste mixers made it impossible for them to be used for producing small experimental paste batches. Therefore to enable the trial to be performed, an experimental paste mixer was developed. It is a scaled down replica of the on-line mixers and is capable of producing paste batches of up to 100 kg.

#### 5.1 THE PROPERTIES USED TO ASSESS LEAD OXIDE QUALITY

Two properties measured off-line are used to assess the quality of freshly produced lead oxide powder. These are free lead (specification 20 to 28%) and apparent density (specification 0.95 to 1.25 g/cm<sup>3</sup>). Another property which could also characterise lead oxide powder and affect its properties is its age.

For example, lead oxide produced at the oxide mill is conveyed to storage silos at the pasting area. It is either stored for several days before use or used within a couple of hours of being produced. The variation in the time of storage (referred to as lead oxide age) may possibly have a serious affect on both the life expectancy and performance of the active material.

To determine what combination of the three lead oxide properties is needed to produce a paste density of  $4.10 \text{ g/cm}^3$  required a series of experimental optimisation tests to be performed. The procedure involved producing a series of experimental paste batches to determine the optimum combination of free lead, apparent density and age. Three possible experimental design techniques were considered.

## 5.2 EXPERIMENTAL OPTIMISATION TECHNIQUES<sup>16,17,18</sup>

The three approaches considered were:

### 5.2.1 The classical approach

A possible approach to determining the optimum combination is to use the classical search approach. This is a one-dimensional test (only one property is varied at a time). To determine the optimum

combination, the following series of tests would have to be performed.

Firstly, a series of experiments would have to be performed in which the free lead is varied from 20 to 28%, while apparent density and age are kept constant (these properties can be set at any values). In each case the composition of paste would be determined and an optimum free lead would be obtained.

A second series of paste composition tests would be performed in which the free lead would be set up at its optimum value, but this time the apparent density would be varied from 0.95 to 1.25 g/cm<sup>3</sup>. Again, the age would remain constant. Under these conditions, the optimum apparent density would be found.

Finally, a series of tests would be performed where age is varied from fresh lead oxide powder to that which has been stored for several days, both the free lead and the apparent density values are set up at their optimum values. The series of tests would then have to be repeated again starting at the apparent optimum and again varying free lead, apparent density and age. These interactions are repeated until successive optimums are sufficiently similar to indicate that no further improvement is possible. The local optimum has then been found. This approach

to the optimisation of the lead oxide properties is clearly very tedious. Also the classical approach assumes that the three properties affect the paste composition in an independent fashion. This might not be true. For example, it could be found that at a free lead of 21%, the optimum apparent density is 1.20 g/cm<sup>3</sup>. However, at a different free lead value the optimum apparent density might not be 1.20 g/cm<sup>3</sup>. These properties may affect the paste composition in an interactive fashion and any conditions (local optimum) that are established using this series of experiments might not actually be the global optimum. If the first series of experiments were started at different conditions, a different set of optimum results might be obtained. For these reasons the classical approach for determining the optimum combination of lead oxide properties was not used.

#### 5.2.2 Full factorial design

The three properties used to assess lead oxide quality can be divided into three levels - bottom, middle and top specification levels. Table 5(i) represents the specification levels for each property.

Table 5(i)      Lead oxide properties for paste composition tests

Property	Specification Range		
	Level 1	Level 2	Level 3
Free lead (%)	Top 27 - 29	Middle - 24 - 26	Low 20 - 23
Apparent density (g/cm <sup>3</sup> )	Top 1.20 - 1.3	Middle 1.10 - 1.20	Low 0.95 - 1.10
Age (Hours)	Warm 2	Fresh 24	Stored 72

Table 5(i)

If paste compositions are measured for all possible combinations of the chosen lead oxide property levels, the tests are referred to as a complete factorial design (or a grid search). The total number of combinations of property specification levels which could be tested are represented in Table 5(ii).

Table 5(ii)      The total number of lead oxide property specification levels which could be tested

Number of Tests	Lead oxide quality specification
1	High Free Lead High apparent density Fresh
2	High Free Lead High apparent density Stored
3	High Free Lead High apparent density Warm
4	Middle Free Lead High apparent density Fresh
5	Middle Free Lead High apparent density Stored
6	Middle Free Lead High apparent density Warm
7	Low Free Lead High apparent density Fresh
8	Low Free Lead High apparent density Stored
9	Low Free Lead High apparent density Warm
10	High Free Lead Middle apparent density Fresh
11	High Free Lead Middle apparent density Stored
12	High Free Lead Middle apparent density Warm
13	Middle Free Lead Middle apparent density Fresh
14	Middle Free Lead Middle apparent density Stored
15	Middle Free Lead Middle apparent density Warm
16	Low Free Lead Middle apparent density Fresh
17	Low Free Lead Middle apparent density Stored
18	Low Free Lead Middle apparent density Warm
19	High Free Lead Low apparent density Fresh
20	High Free Lead Low apparent density Stored
21	High Free Lead Low apparent density Warm
22	Middle Free Lead Low apparent density Fresh
23	Middle Free Lead Low apparent density Stored
24	Middle Free Lead Low apparent density Warm
25	Low Free Lead Low apparent density Fresh
26	Low Free Lead Low apparent density Stored
27	Low Free Lead Low apparent density Warm

Table 5(ii)

There are twenty-seven possible tests. The full factorial (grid search) design for determining the optimum lead oxide quality is the complete opposite of the classical approach in which the paste composition would be investigated for each property in turn, while all other properties are held at a constant level.

The benefits for using a factorial design rather than a classical design are:

- (i) The factorial experiment details and estimates any interaction, which the one at a time experiments cannot do (finds the global optimum).
- (ii) If the effects of the properties are additive, then the factorial design needs fewer measurements than the classical approach in order to give the same precision.

A problem with complete factorial experiments is that the number of experiments required rises rapidly with the number of properties and with the number of steps into which each parameter is divided. For example if the specification was divided into 10% steps then above experiment would require 1000 tests. However, by assuming that higher order interactions are negligible compared to the main effects and factor interaction effects, a suitable fraction of all possible combinations of factor levels is sufficient to provide an estimate of the main and factor interaction effects.

Such an experimental design is called an incomplete

or fractional factorial design. Therefore, as a result of being able to perform a smaller number of experiments but still obtain the same results as performing a full factorial, the fractional factorial design was chosen.

### 5.2.3 Fractional Factorial Design<sup>18</sup>

An exponent of fractional factorial design is Dr. Genichi Taguchi, a Japanese statistician, who has combined both engineering and statistical methods to achieve rapid improvements in costs and quality by optimising product design and production processes. Taguchi's approach to experimental design utilises techniques that are cost effective and directly applicable to problems and requirements of modern industry. Taguchi has popularized a very direct way to examine many properties in an economical manner (the use of orthogonal arrays).

Full factorial designs cover all possible test conditions, for example, three factors at three levels would require twenty-seven experiments. Figure 5(i) represents the full factorial design.



Figure 5(i)      Orthogonal array  $L_{27}(3^3)$

Number/Column (Test Number)	Factor 1	Factor 2	Factor 3
1	1	1	1
2	1	1	1
3	1	1	1
4	1	2	2
5	1	2	2
6	1	2	2
7	1	3	3
8	1	3	3
9	1	3	3
10	2	1	2
11	2	1	2
12	2	1	2
13	2	2	3
14	2	2	3
15	2	2	3
16	2	3	1
17	2	3	1
18	2	3	1
19	3	1	3
20	3	1	3
21	3	1	3
22	3	2	1
23	3	2	1
24	3	2	1
25	3	3	2
26	3	3	2
27	3	3	2

Figure 5 (i)

The idea of using orthogonal arrays for the design of experiments was studied independently in the United

States and Japan during Word War II. Taguchi recommends the use of orthogonal arrays for assigning experiments. There are a number of different orthogonal arrays and the type used depends on the number of properties (factors) and levels which are to be tested.

In an orthogonal array, each factor at each level appears the same number of times. In any pair of columns, each factor at each level appears in combination with the other factor at each level. Each combination appears the same number of times. The various combinations of factor levels are said to be balanced. Orthogonal arrays as a result of the balanced combination of property levels remove the necessity for full factor factorial experiments being performed (full factorials only need to be used if the factors are believed to interact). Full factorial designs cover all possible test conditions, for example, three factors at three levels would require twenty-seven experiments (see Figure 5(i)), however for every pair of columns, all combinations of levels occur and they occur an equal number of times in a fractional factorial design with only nine experiments. (Using fractional factorial with only nine experiments there is an assumption that no interaction occurs between factors). In Section 5.5 this assumption is checked.

Figure 5(i) is termed orthogonal array  $L_{27}$ . The number to the left of each row is called the experiment number and it runs from 1 to 27. The vertical alignments are termed columns of the orthogonal array and every column consists of nine each of the numbers 1, 2 and 3. Since the combinations of the numerals of any column and those of any other column are made up of the numerals 1, 2 and 3 there are nine possible combinations.

When each of the two columns consists of the numeral 1, 2 and 3 and the nine combinations (11), (12), (13), (22), (21), (23), (33), (31) and (32) appear with the same frequency, we say that these two columns are balanced, or orthogonal.

As a result of each combination being balanced, the orthogonal array ( $L_{27}$ ) can be reduced, so that only nine tests need to be performed in order to determine the optimum combination of lead oxide properties. Figure 5(ii) represents the reduced array.

Figure 5(ii) Orthogonal array ( $L_9$ )

Number/column	1	2	3
1	1	1	1
2	1	2	2
3	1	3	3
4	2	1	2
5	2	2	3
6	2	3	1
7	3	1	3
8	3	2	1
9	3	3	2

Figure 5(ii)

A major feature of Taguchi's utilisation of orthogonal arrays is the reproducibility of the conclusions drawn from small scale experiments. The steps which have to be undertaken whilst performing a Taguchi design are:

- (a) Define the problem, i.e. a clear statement of the problem to be solved.
- (b) Determine the objective.
- (c) Determine the levels and values for each property.
- (d) Design the experiment, i.e. select the appropriate orthogonal array for the number of properties.
- (e) Conduct the experiment and collect data.

- (f) Analyse data, i.e. average response tables and graphs.
- (g) Interpret results and select optimum levels of properties.
- (h) Run a confirmatory experiment to verify predicted results. If results are not confirmed or are unsatisfactory, additional experiments are required.

The Taguchi approach to fractional design required that the trial be performed using two samples for each combination of lead oxide properties. Hence eighteen experimental batches of paste were required. Repeating each mix would ensure that results could be verified.

For each trial mix, 50 kg batches of paste were produced in the experimental mixer. The quantities of ingredients used are shown in Table 5(iii).

Table 5(iii) Quantity of ingredients used to produce 50 kg batches of paste

Ingredients	Quantity
Lead oxide	50 kg
Water	6.5 litres
1.4SG sulphuric acid	6.5 kg
Polypropylene fibres	15 grams

Table 5(iii)

### 5.3 DEVELOPMENT OF THE STIFFNESS TEST FOR ASSESSING PASTE COMPOSITION

To measure paste stiffness, equipment had to be designed which enabled the paste to be subjected to a range of forces. The force was applied using a tensile strength meter (T.S.M.) with a maximum force capability of 2,000 newtons(N). The instrument was equipped with an RS232 communications link, which enabled it to be interfaced to a microcomputer. Software purchased with the T.S.M. allowed the forces at which paste flows to be displayed as profiles of force (N) against piston movement (mm). All profiles were stored for further analysis.

#### 5.3.1. OUTLINE OF THE SAMPLE HOLDER REQUIREMENTS

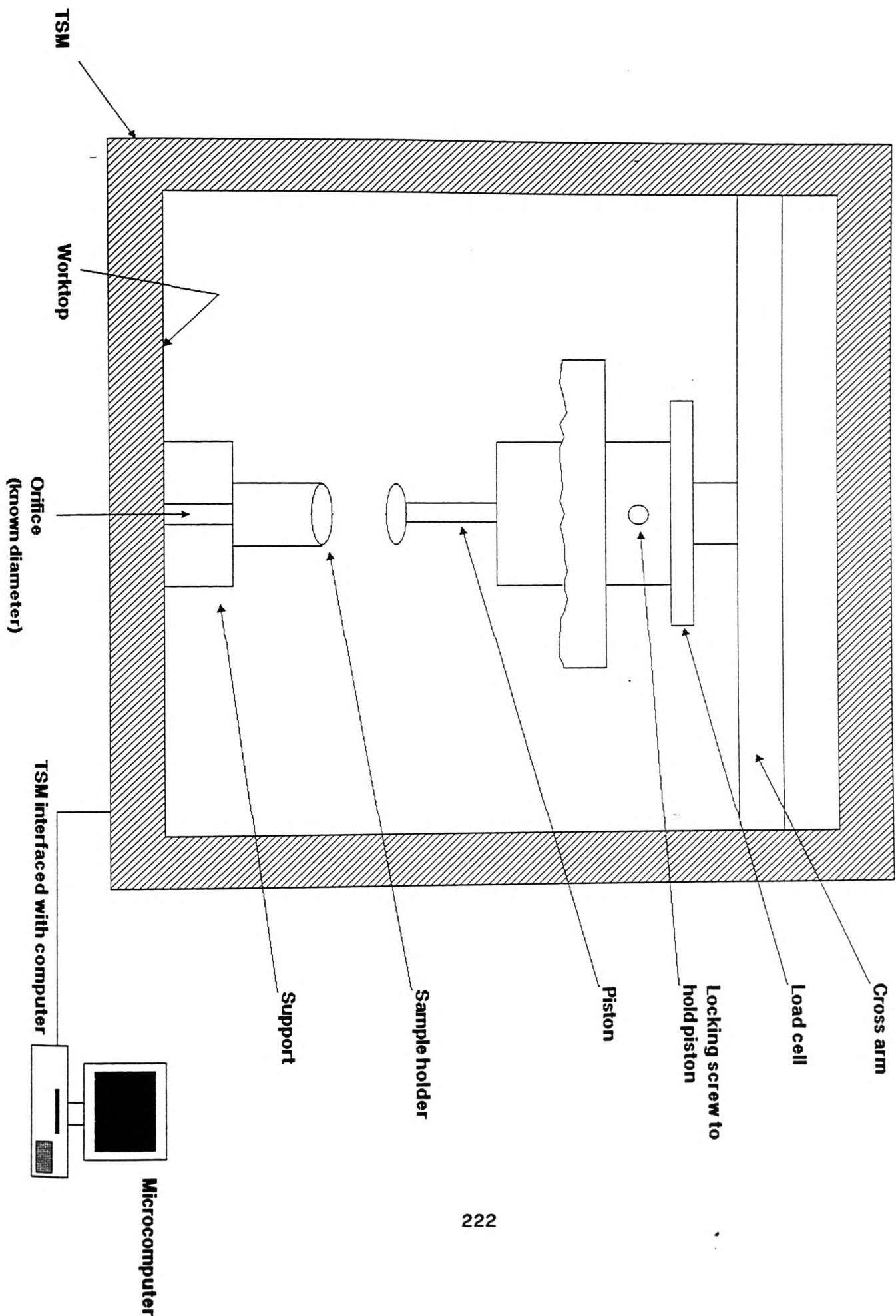
The major problem in developing the test was the design of the sample holder. A cylindrical shape was considered. At one end was an orifice of known diameter through which paste was forced by a piston. The piston was a tight sliding fit inside the sample holder.

The piston was attached to the cross arm of the T.S.M. and a load cell positioned above the piston measured the compression forces applied to paste samples. Support for the sample holder was provided

by the working area on the T.S.M. The test, although off-line, was completely automated. Figure 5(iii) illustrates the equipment.

Each paste sample was uniformly packed into the holder to eliminate variations, such as air gaps, which could lead to non-reproducible results.

**Figure 5 (iii)** Diagrammatic representation of the equipment used to measure paste stiffness





Designing the stainless steel holder proved more difficult than expected. A number of prototypes were discarded. To assess paste stiffness, samples had to be uniformly packed into a holder. The sample holder had to be designed to enable paste samples to be subjected to an applied force from a piston attached to the cross arm of a T.S.M. The movement of the piston through the cylinder gave an estimate of the stiffness of the paste (the paste flow characteristics).

The sample holder had to be able to extrude the compressed paste as the piston moved within it. An orifice had to be located at the base of the holder.

Designing the sample holder required:

- (i) a precise fit for the plunger into the sample holder (to enable a uniform compression force to be applied to paste samples).
- (ii) determination of the orifice diameter.
- (iii) determination of the base angle of the sample holder bottom in order to allow the

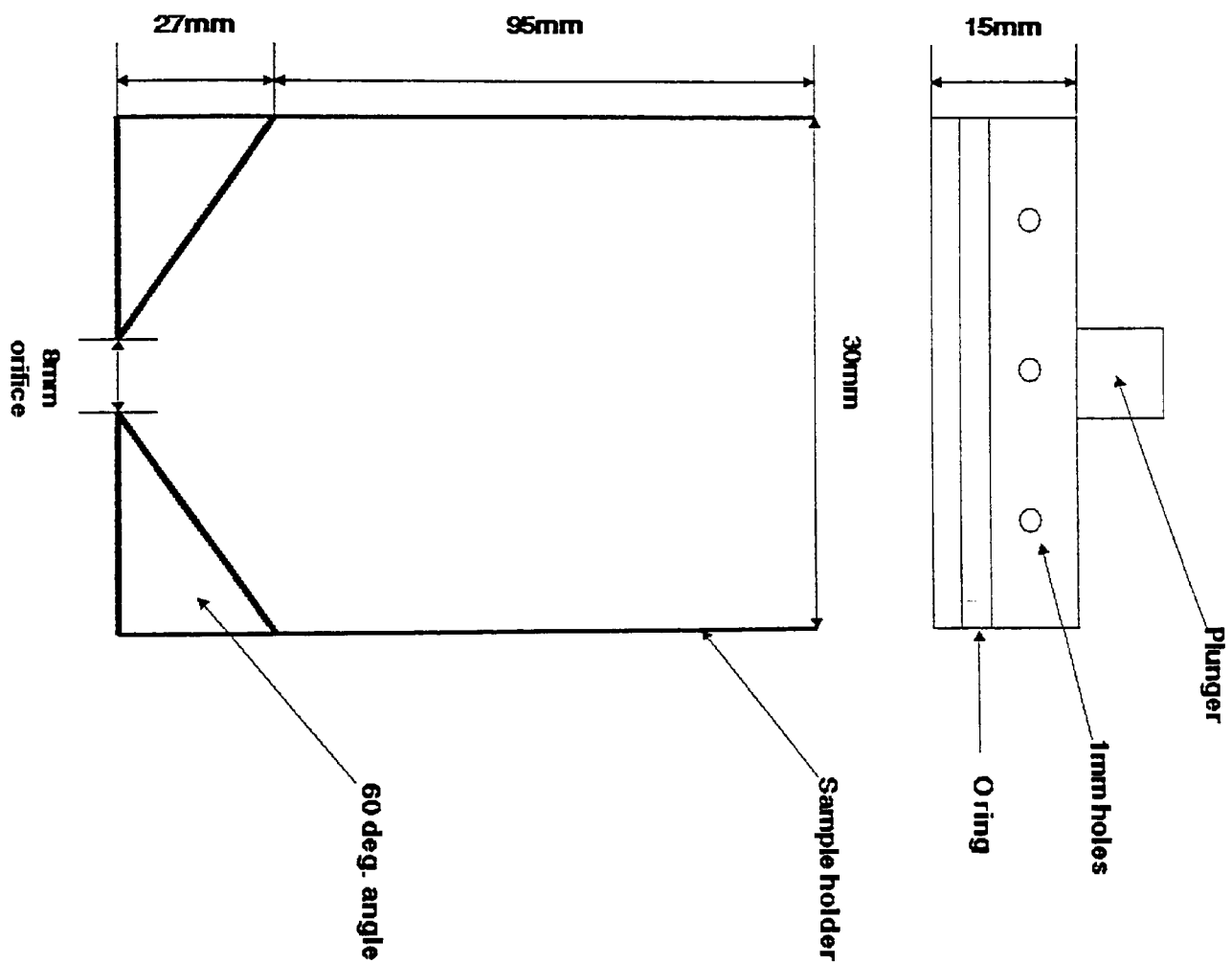
compressed paste to be extruded.

Extrusion of the compressed paste enabled the stiffness properties to be measured over a large force range. Figure 5(iv) shows the holder design which was finally used.

The steps in the development of the holder were:

- (i) The first prototype piston was 35 mm long with a head diameter of 30 mm. The holder was 35 mm long with a diameter of 30 mm. The orifice was 4 mm in diameter. This model was unable to extrude paste.
- (ii) The second prototype had the same holder dimensions, but the piston dimensions were changed. The length was increased to 45 mm but the head diameter remained the same. To relieve air pressure, three 1 mm holes were drilled in the head. However, the model was still unable to extrude paste.

**Figure 5 (iv)     Prototype holder which best suited the flow characteristics of the company's paste**



**Fig. 5 (iv)**

- (iii) In the third prototype, the orifice was changed to 8 mm and 0.02 mm was machined off the piston head. To create a seal with the holder surface, an O-ring was fitted on the piston head. This model was still unable to extrude paste.
- (iv) The final modifications involved tapering the base to create an angle which allowed paste to be extruded. Tapering the base of the sample holder had the effect of reducing the shear force required to extrude the compressed paste.

Prototypes were designed with angles ranging from 15 to 60 degrees. The only model which allowed paste to extrude was the 60° angle version.

Having developed a paste holder which allowed the stiffness of freshly mixed paste to be determined, tests were performed to assess the nature of the force profiles which could be obtained.

### 5.3.3 ANALYSIS OF THE REPRODUCIBILITY OF PASTE STIFFNESS RESULTS

Initial trial runs were performed and force profiles were graphically displayed using the microcomputer.

Initially five positive paste samples were analysed. Each sample produced a characteristic force profile. Figure 5(v) shows the profile obtained.

The profiles consist of three sections (slopes). Slope A extends over the range of 0 to 3 mm. The force range in this region is from 0 to 500 N and equates to the force required to compress the paste and to commence extrusion. Slope B extends over the range of 5 to 27.5 mm. It is only in this region that the compression forces extrude paste. Therefore, it is this region which is utilised to characterise paste composition in terms of stiffness. The force range is from 500 to 1,400 N. Slope C extends over the range of 27.5 to 55 mm. Data obtained here could not be used to characterise paste stiffness, because, as the piston travelled further along the holder, paste is starting to block up in the holder base. This results in high force values which are not considered true representations of paste stiffness. The force range is from 1,400 to 2,000 N.

Having established that the test worked, additional tests were performed to determine whether the experimental procedure was capable of reproducible results.

Figure 5(v) Characteristic stiffness profile for positive paste

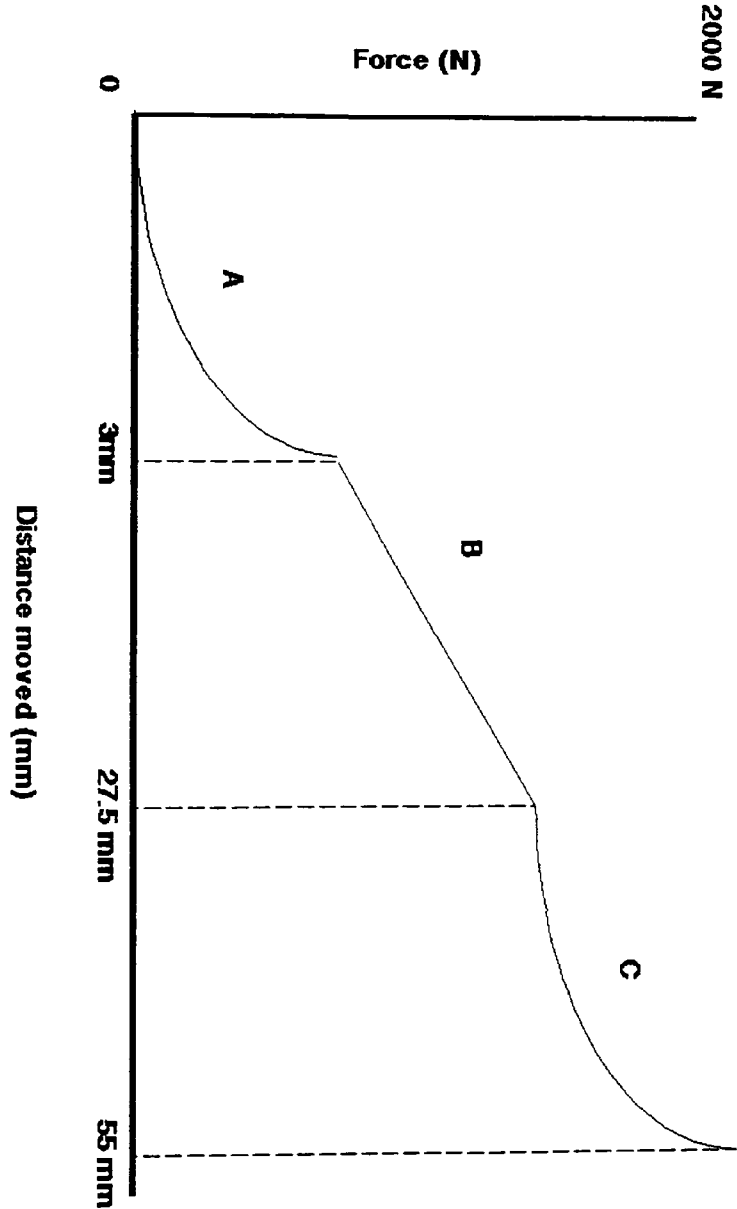


Fig. 5 (v)

To test reproducibility, 2 kg samples of positive paste were divided into five portions. The stiffness test was performed on each portion and the mean and standard deviation of each 2 kg paste sample was calculated. Table 5 (iv) shows the results.

The results of the tests demonstrated that the procedure used for measuring paste stiffness was capable of producing reproducible results. The holder could be uniformly packed to ensure that consistent results were obtained.

Table 5(iv)      Reproducibility of the paste stiffness results

Test Number	Paste stiffness (N/mm) Gradient sector B	Mean stiffness (N/mm)	Standard deviation
1	14 14 13 13 14	13	0.5
2	21 20 20 21 21	21	0.5
3	19 19 18 19 18	19	0.5
4	23 22 23 23 22	23	0.5
5	15 14 14 15 15	15	0.5

Table 5(iv)

#### 5.4

#### DEVELOPMENT OF THE EXPERIMENTAL PASTE MIXER

Originally the experimental paste batches were to be prepared in the company's large on-line paste mixers. Unfortunately due to production demands imposed on the mixers, neither could be used for development trials. In order to carry out the trial and determine the effect of varying lead oxide qualities on paste composition, the Technical Development Director of the company allowed an experimental paste mixer to be purchased. It was an exact scaled-down version of the on-line paste mixers and was capable of producing a maximum paste batch quantity of 100 kg.

##### 5.4.1

#### DESIGN OF THE EXPERIMENTAL PASTE MIXER

The design of the experimental paste mixer was based on the larger on-line mixers. Each design feature of the on-line mixers had to be incorporated into the experimental mixer.

The following features and process operations of the production mixers had to be considered. The sequential steps for producing paste in the on-line mixers are automatically controlled by a program logic controller (PLC). The first step involves weighing the required quantity of lead oxide powder



in a pre-feeder. On achieving the required weight, a butterfly valve in the base of the pre-feeder opens, releasing the weighed lead oxide powder into the mixing bowl. The required quantities of water and sulphuric acid are added by sprinklers positioned underneath the mixing bowl lid (Additives are included prior to lead oxide addition).

The requirements for producing paste, involve weighed quantities of ingredients being added into the mixing bowl at set time intervals. The total time period for the mixing cycle is fifteen minutes. The mixing time schedule is shown in Table 5(vi).

Table 5(vi) Sequence of addition times and ingredient quantities used for positive paste mixing

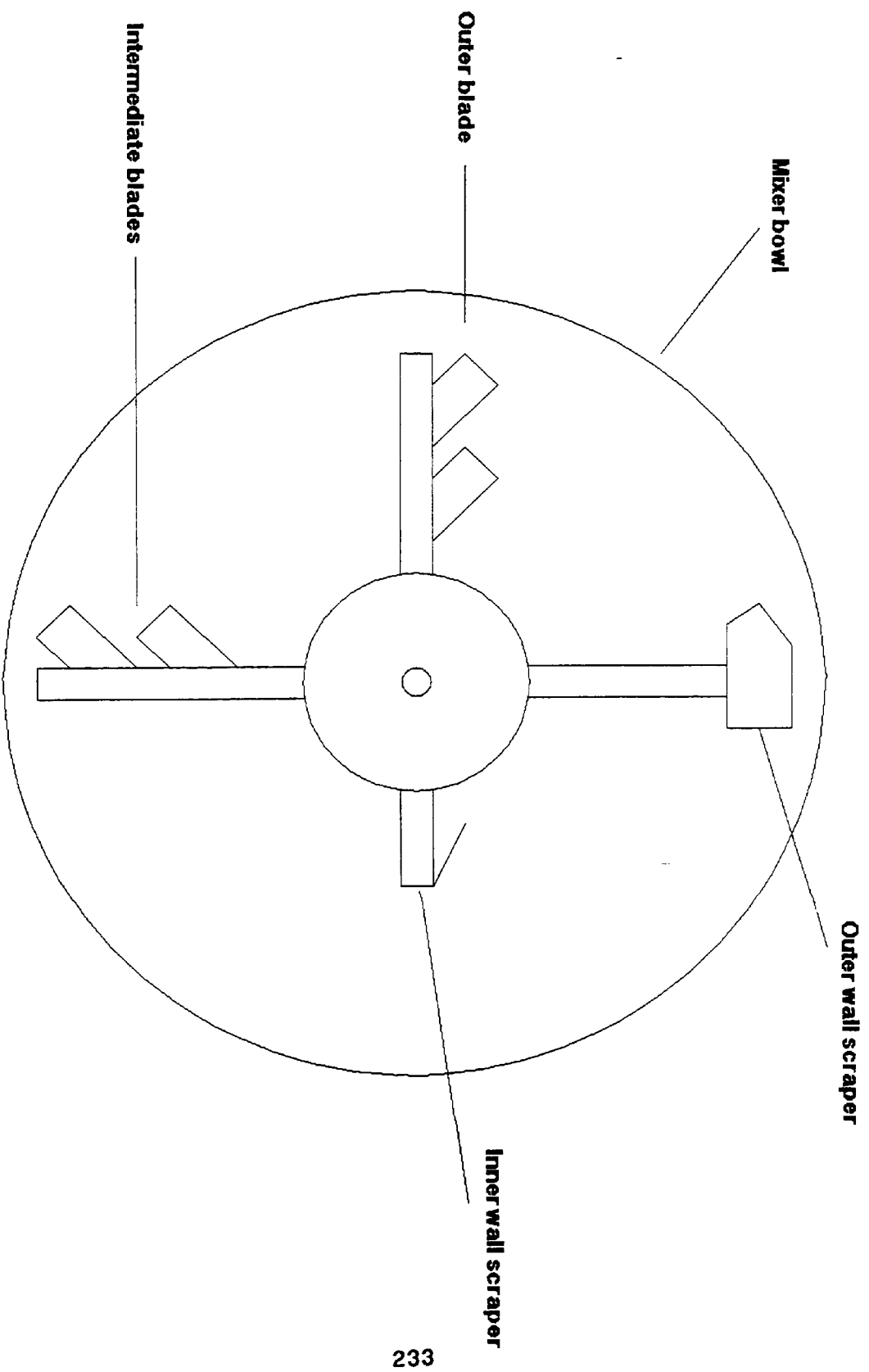
Ingredients	Quantity	Duration
Lead oxide powder	500 kg	50 seconds
Dry mix	—	10 seconds
Water addition	65 litres	33 seconds
Wet mix	—	3 minutes
Acid addition	68 kg	6 minutes 40 seconds
Final mix	—	3 minutes 47 seconds

Table 5(vi)

The dimensions of the mixing bowl are also important.

The experimental mixers had to be large enough to ensure uniform mixing occurred and that sufficient air cooling over the paste surface was obtained. Both of the production mixers have bowl dimensions of six feet diameter with a depth of two feet. Inside each bowl, mixer blades ensure thorough mixing. Figure 5(vi) shows the blade design.

**Figure 5 (vi)    Blade arrangement in the mixing bowl**



**Fig. 5 (vi)**

The blades are angled so that each one feeds paste into the path of the next. The drive system for the mixing blades in the full size mixers consist of a forty horsepower motor used with a 40:1 reduction gear box. The speed is set at thirty-eight revolutions per minute (rpm). To ensure that paste temperature remains below the recommended setpoint of 60°C, a sustained airflow has to be maintained over the paste surface. A thermocouple in the base of the bowl monitors the reaction temperature. Paste temperature after mixing is usually 35 to 40°C.

#### 5.4.2. Design Requirements for the experimental paste mixer

The experimental paste mixer had to be designed to enable 100 kg batches of paste to be produced. The initial step was to determine the dimensions of the bowl. The following calculations were used. The first step was to determine the volume occupied by the on-line paste mixers. This was calculated using Equation 5(i).

$$\begin{array}{l} \text{Volume} \\ \text{of on-line} \\ \text{mixing bowl} \end{array} = r^2 h$$

where:  $r$  = radius of bowl  
 $h$  = depth of bowl

Equation 5(i)

The on-line mixers were capable of producing 1000 kg size batches of paste. The experimental mixer only requires one tenth of this volume as only 100 kg size paste batches are required to be produced. To calculate the diameter and height of the experimental mixing bowl, an assumption was made for the mixing bowl height. It was decided to give the mixing bowl a height of 30 cm ( This ensured that there was plenty of room between the paddles and the bottom of the lid).

The lid had a viewing hatch and it was felt that an accident could occur if the hatch was only just above the paddles. By making the bowl height 30 cm, removed the likelihood of an accident occurring. Hence knowing the volume and height, the diameter of the bowl could be calculated using Equation 5(i). A diameter of 85 cm was calculated.

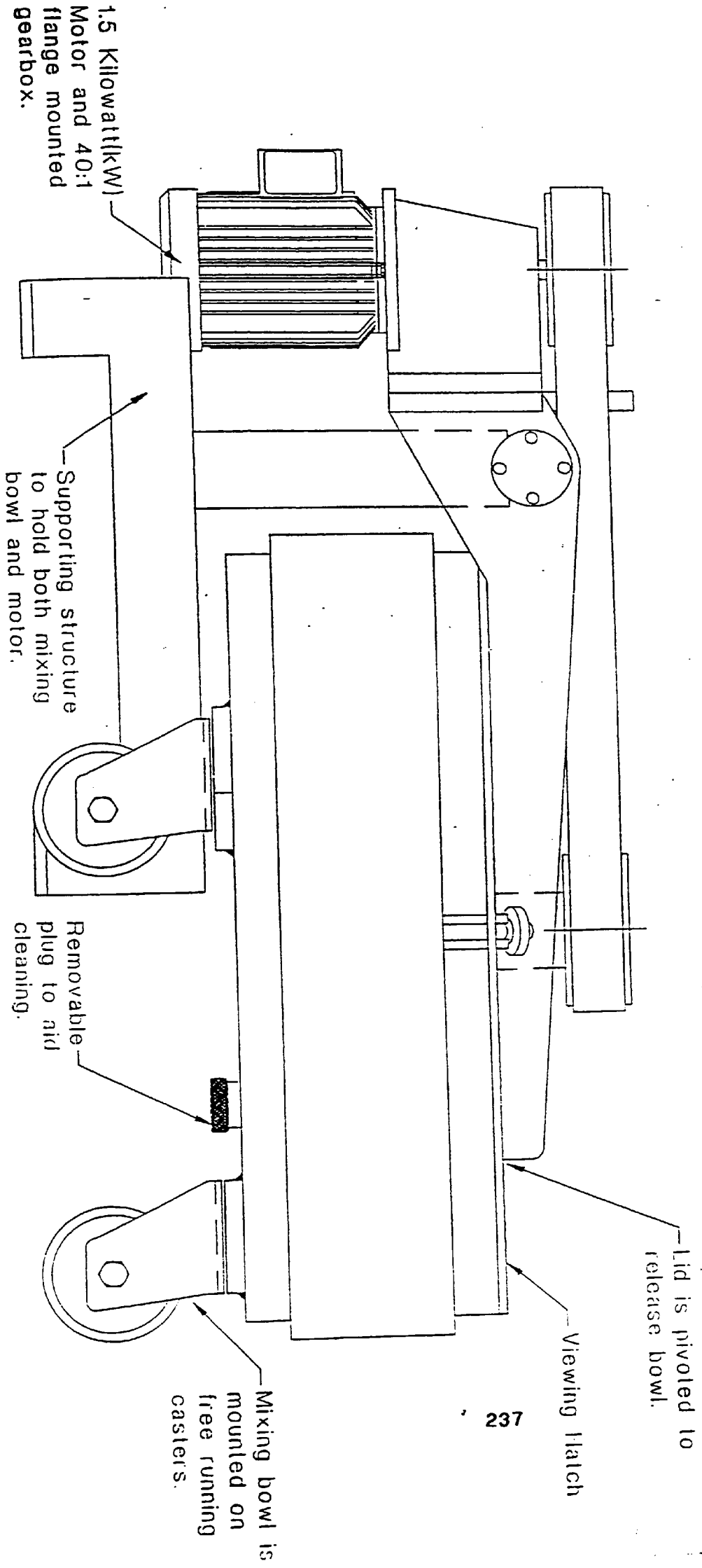
The blade design was copied exactly and scaled down to ensure that each blade was correctly positioned and angled to feed paste into the path of another. Paste temperature was controlled by air cooling. A thermocouple located in the bowl base monitored temperature. A drive system comprising of a 2.5 kw motor with a 40:1 reduction gear box with a chain drive and appropriate pulley ensured that the torque was similar to the on-line paste mixers (The design

requirements for the motor size and ratio for the reduction gear box were calculated by the engineering company who manufactured the experimental mixer).

The ingredient addition times for trial paste batches were kept the same as the 500 kg paste mixes (See Table 5(vi)). However, as no PLC could be used to control the ingredient additions, the following procedure had to be performed. Both lead oxide and additives were added first. Water and acid were weighed prior to starting and were added from beakers at the required times through the viewing hatch in the lid. Mixes were transferred to the pasting hopper by shovelling.

The design of the experimental paste mixer is shown in Figure 5(vii).

Figure 5 (vii) Experimental paste mixer design.



The experimental mixer was tested to determine if it could produce paste with similar composition, i.e. density, stiffness and appearance characteristics, as both of the on-line mixers.

Determination of this involved producing paste batches on both the experimental and on-line mixers from the same lead oxide stream. A set procedure was used to ensure that the same lead oxide samples were used for each paste mix. This involved removing a 100 kg sample, from the butterfly valve in the lead oxide hopper situated above the on-line paste mixers, prior to dumping 500 kg of lead oxide into the on-line mixing bowl.



Both the trial and production mixes were performed at the same time. Table 5(vii) shows the comparison between the experimental and on-line paste mixes.

Table 5(vii) Comparison between paste produced in the experimental and on-line mixers

Paste Mixer	Density (g/cm <sup>3</sup> )	Mean Density (g/cm <sup>3</sup> )	Std Deviation of Density (g/cm <sup>3</sup> )	Stiffness (N/mm)	Mean Stiffness (N/mm)	Std Deviation of Stiffness (N/mm)
Production Mixer	4.05,4.06, 4.06 4.06	4.057	$5 \times 10^{-3}$	14,14,13,14	13.75	0.5
Experimental Mixer	4.06,4.06, 4.06,4.06	4.06	0	14,13,13,14	13.50	0.57
Production Mixer	4.11,4.11, 4.11,4.11	4.11	0	17,16,16,16	16.25	0.5
Experimental Mixer	4.11,4.11, 4.11,4.11	4.11	0	16,17,17,16	16.50	0.57
Production Mixer	4.09,4.08, 4.08,4.09	4.085	$5.77 \times 10^{-3}$	25,24,25,25	24.75	0.5
Experimental Mixer	4.09,4.09, 4.09,4.08	4.087	$5 \times 10^{-3}$	25,25,25,25	25.00	0
Production Mixer	4.05,4.05, 4.05,4.05	4.05	0	14,14,14,14	14.00	0
Experimental Mixer	4.05,4.05, 4.05,4.05	4.05	0	14,14,14,14	14.00	0
Production Mixer	4.18,4.18, 4.18,4.17	4.177	$5 \times 10^{-3}$	22,21,22,22	21.75	0.5
Experimental Mixer	4.17,4.17, 4.18,4.18	4.175	$5.77 \times 10^{-3}$	21,22,21,22	21.50	0.57

Table 5(vii)

Comparison of the means and standard deviation values for both density and stiffness results revealed that the experimental mixer was capable of producing batches of paste with identical composition to the larger production mixers.

TESTS TO DETERMINE THE EFFECT OF LEAD OXIDE QUALITY  
ON PASTE COMPOSITION

The aim was to determine what combination of lead oxide properties were capable of producing a positive paste density of  $4.10 \text{ g/cm}^3$ . Trial batches of paste were manufactured in the experimental mixer from lead oxide powder of varying age, free lead and apparent density. The stiffness of each paste batch was measured.

A fractional factorial design experiment was used to determine the optimum combination of lead oxide powder. For each trial batch, paste density was measured after fifteen minutes of mixing. The stiffness of each paste batch was determined by collecting four samples, one from each quarter of the mixing bowl. To prevent water loss, the samples were kept in sealed bags until they were analysed. The mean of the four samples was calculated to represent the stiffness of the paste batch tested.

Table 5(viii) represents the paste composition results which were obtained using different combinations of lead oxide properties for each of the nine experimental mixes.

Table 5(viii) Paste composition results obtained using the combination of lead oxide properties given by the fractional factorial design array for three factors at three levels

Mix No.	Free Lead (%)	App. Density (g/cm <sup>3</sup> )	Age (Hours)	Mix Time (Minutes)	Paste Density (g/cm <sup>3</sup> )	Paste Temp. (°C)	Stiffness (N/mm)	Mean Stiffness (N/mm)
1	22	1.18	2	15	4.09	28	24,25,25, 24,	25
2	29	1.18	24	15	4.17	30	22,22,22, 21	22
3	25	1.29	24	15	4.08	31	23,23,23, 23	23
4	22	1.28	72	15	4.11	25	14,15,15, 15	15
5	27	1.38	2	15	4.18	32	13,13,13, 13	13
6	23	1.12	72	15	4.04	31	26,27,27, 28	27
7	24	1.06	2	15	4.11	32	17,16,16, 15	17
8	21	1.06	24	15	4.09	32	25,25,25, 24	25
9	26	1.10	72	15	4.06	32	14,14,14, 14	14

Table 5(viii)

Each mix was performed twice. Table 5(ix) shows the second set of results.

Table 5(ix) Second set of paste composition results obtained using the same combinations of free lead, apparent density and age of lead oxide powder

Mix number	Paste density (g/cm <sup>3</sup> )	Stiffness (N/mm)	Mean Stiffness (N/mm)
1	4.08	24, 24, 24, 24	24
2	4.16	22, 22, 23, 24	22
3	4.07	23, 23, 22, 23	23
4	4.10	14, 13, 14, 14	14
5	4.17	12, 12, 12, 13	12
6	4.03	26, 25, 26, 26	26
7	4.13	19, 19, 20, 19	19
8	4.08	24, 24, 24, 24	24
9	4.08	16, 16, 16, 17	16

Table 5(ix)

Similar paste composition results (i.e. density and stiffness values) were obtained for both trials. To determine the effect of the different lead oxide factor levels on paste composition, statistical analysis techniques were used (average response tables and graphs).

#### 5.5.1 ANALYSIS OF PASTE DENSITY AND STIFFNESS RESULTS

For this test, three control factors at three levels were selected. The characteristic properties chosen to represent paste composition were density and stiffness. The results of both tests were entered into the orthogonal arrays. Figure 5(viii) represents the orthogonal array containing both selected characteristic data sets.

Figure 5(viii) Orthogonal array containing both density and stiffness data

Factor A level Free lead	Factor B level Apparent density	Factor C level Age	Stiffness data	Density data
1	1	1	13,12	4.17, 4.18
1	2	2	22,20	4.16, 4.17
1	3	3	14,16	4.08, 4.06
2	1	2	23,22	4.08, 4.09
2	2	3	27,26	4.04, 4.05
2	3	1	17,19	4.13, 4.12
3	1	3	15,14	4.10, 4.11
3	2	1	25,24	4.08, 4.09
3	3	2	25,27	4.05, 4.04

Figure 5(ix)

Stiffness and density results were analysed

separately.

#### 5.5.2 INVESTIGATION OF PASTE STIFFNESS DATA<sup>18</sup>

The calculations<sup>18</sup> used to assess stiffness were as follows. Equation 5(ii) was used to calculate an average value for the stiffness data.

##### Equation 5(ii)

$$\begin{array}{llll} \text{Number of data points} & n & = & 18 \\ \text{TOTAL of the data} & T & = & \{ 361 \\ \text{Average of the data} & \overline{T} & = & \frac{T}{n} = 20.05 \end{array}$$

To compare factor levels, a response table was constructed. The average response for each factor level had to be calculated. Equation 5(iii) shows how the average responses were calculated.

##### Equation 5(iii)

$$\begin{array}{llll} \overline{A_1} & = & \frac{13+12+20+22+14+16}{6} & = 16 \\ \overline{A_2} & = & \frac{23+22+26+27+19+17}{6} & = 22 \\ \overline{A_3} & = & \frac{15+14+25+24+27+25}{6} & = 21 \\ \overline{B_1} & = & \frac{13+12+22+23+14+15}{6} & = 16 \end{array}$$

$$\begin{aligned}
\overline{B_2} &= \frac{22+20+26+27+25+24}{6} = 24 \\
\overline{B_3} &= \frac{16+14+17+19+25+27}{6} = 19 \\
\overline{C_1} &= \frac{13+12+17+19+24+25}{6} = 18 \\
\overline{C_2} &= \frac{22+20+23+22+27+25}{6} = 23 \\
\overline{C_3} &= \frac{14+16+27+26+14+15}{6} = 18
\end{aligned}$$

Having calculated the average response for each factor level, the next step was to estimate the main effect of each factor. The main effect is the average effect of each factor over "all" conditions of the other variables. Equation 5(iv) reveal how the main effects were calculated. Each factor has three average response values (one for each level). The main effect for each factor is calculated by averaging the two average response values which are closest together and subtracting this figure from the remaining average response value. This result is the main effect of the particular factor under investigation.

Equation 5(iv)

Factor A

$$\text{Main effect A} = \frac{\overline{A_2} + \overline{A_3}}{2} - \overline{A_1} = 5$$

Factor B

$$\text{Main effect B} = \overline{B_2} - \frac{\overline{B_1} + \overline{B_3}}{2} = 7$$

Factor C

$$\text{Main effect C} = \overline{C_2} - \frac{\overline{C_1} + \overline{C_3}}{2} = 5$$

Table 5(x) represents the data for main effects and average responses.

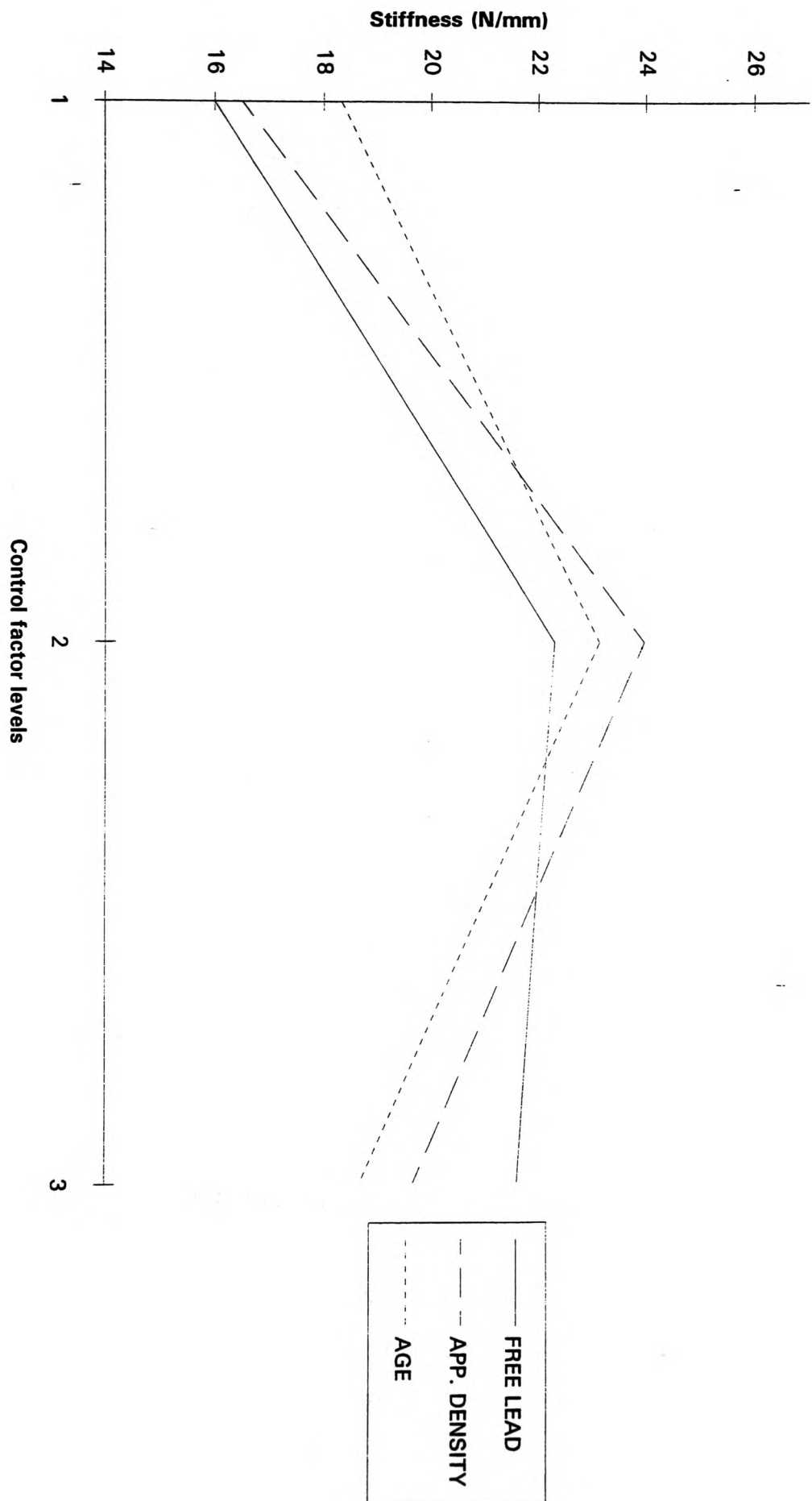
Table 5(x)      Response table for stiffness data

	Free lead (factor A)	Apparent density (factor B)	Age (factor C)
Level 1	16	16	18
Level 2	22	24	23
Level 3	21	19	18
Main effect	5	7	5

Table 5(x)

Having constructed the response table it was possible to estimate the strength of the effect for each factor by comparing main effects. The comparison revealed that the factors appeared to have similar effects for stiffness. The next step was to plot the response charts (graphically represent factor effects). Figure 5(ix) represents the response chart for the stiffness data.

Figure 5(ix) Response chart for stiffness data





Analysis of the chart allowed selection of the optimal factors which were necessary to produce ideal paste composition (in terms of stiffness). The recommendation for optimisation (to produce positive paste with high stiffness) was to use lead oxide powder with middle free lead content (23 to 25%), middle apparent density (1.10 to 1.18 g/cm<sup>3</sup>) and twenty-four hours old.

To check the reproducibility of the results (to check the interaction effects between factors are not significant), an estimate of the response (stiffness) under the recommended condition (A<sub>2</sub>B<sub>2</sub>C<sub>2</sub>) had to be performed. It would be compared with the results of a confirmation run (an experimental run under the optimal condition). The estimate of response (process average) was derived using a principle known as additivity of effects (only "main effects" are significant not "interaction effects").

Equation 5(v) shows the additivity of effects principle used to estimate the process average.

Equation 5(v)

$$\begin{aligned}\bar{U} &= \bar{A}_2 + \bar{B}_2 + \bar{C}_2 - 2\bar{T} \\ &= 22 + 24 + 23 - 2(20) \\ \bar{U} &= 29\end{aligned}$$

where:

$\bar{U}$  = estimate of process average stiffness at the optimal condition

$\bar{T}$  = overall average of the data

The purpose of the confirmation run was to check the reproducibility of results. The run was conducted at condition  $A_2B_2C_2$ . Two runs (mixes) were performed and the results were compared to the predicted process average result. Table 5(xi) represents the comparison of the results.

Table 5(xi) Comparison of the confirmation runs with the predicted process average

Confirmation run		Predicted
Case 1 28.5	Case 2 28	Process Average 29

Table 5(xi)

Analysis of the results revealed that the reproducibility for both cases was very close. Therefore, the experimental results were accepted. If there had been no clear correlation between the estimate of response and the confirmation run under the recommended optimised conditions, the large  $L_{27}$  factorial array would have to be used because significant interaction between factors would have occurred.

The calculations<sup>18</sup> used to assess density were as follows. Equation 5(vi) was used to calculate an average value for the density data.

Equation 5(vi)

Number of data points     $n = 18$

Total of the data         $T = 73.7$

Average of the data       $\bar{T} = \frac{T}{n} = 4.10$

To compare factor levels a response table was constructed. The average response for each factor level had to be calculated. Equation 5(vii) shows how the average responses were calculated.

Equation 5(vii)

$$\bar{A}_1 = \frac{4.17+4.18+4.17+4.16+4.06+4.08}{6} = 4.14$$

$$\bar{A}_2 = \frac{4.0+4.08+4.04+4.05+4.13+4.12}{6} = 4.09$$

$$\bar{A}_3 = \frac{4.11+4.10+4.09+4.08+4.04+4.05}{6} = 4.07$$

$$\overline{B}_1 = \frac{4.17+4.18+4.08+4.09+4.10+4.11}{6} = 4.12$$

$$\overline{B}_2 = \frac{4.16+4.17+4.04+4.05+4.09+4.08}{6} = 4.09$$

$$\overline{B}_3 = \frac{4.08+4.06+4.13+4.12+4.05+4.04}{6} = 4.08$$

$$\overline{C}_1 = \frac{4.17+4.18+4.13+4.12+4.08+4.09}{6} = 4.13$$

$$\overline{C}_2 = \frac{4.16+4.17+4.08+4.09+4.05+4.04}{6} = 4.10$$

$$\overline{C}_3 = \frac{4.08+4.06+4.04+4.05+4.10+4.11}{6} = 4.07$$

Having calculated the average response for each factor level, the next step was to estimate the main effect of each factor. Equation 5(viii) reveals how the main effects were calculated.

#### Equation 5(viii)

##### Factor A

$$\text{Main effect A} = \overline{A}_1 - \frac{\overline{A}_2 + \overline{A}_3}{2} = 0.06$$

##### Factor B

$$\text{Main effect B} = \overline{B}_1 - \frac{\overline{B}_2 + \overline{B}_3}{2} = 0.4$$

##### Factor C

$$\text{Main effect C} = \overline{C}_1 - \frac{\overline{C}_2 + \overline{C}_3}{2} = 0.05$$

Table 5(xii) represents the data for main effects and average responses.

Table 5(xii)     Response table for density data

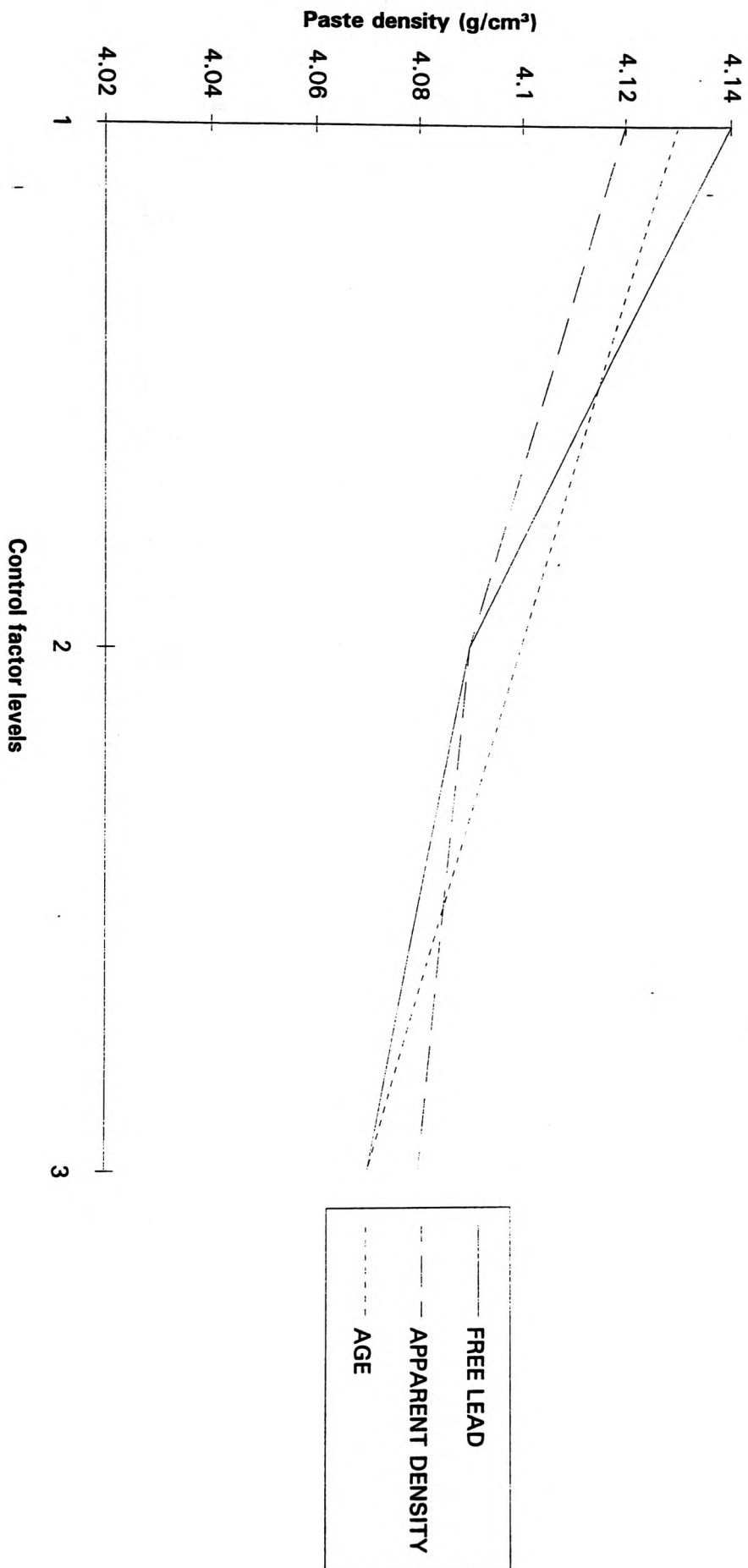
	Free lead (factor A)	Apparent density (factor B)	Age (factor C)
Level 1	4.14	4.12	4.13
Level 2	4.09	4.09	4.10
Level 3	4.07	4.08	4.07
Main effects	0.06	0.04	0.05

Table 5(xii)

Having constructed the response table it was possible to estimate the strength of the effect for each factor by comparing main effects. Analysis of the response table revealed that the factors appeared to have similar effects for density.

The next step was to graphically represent the factor levels. Figure 5(x) represents the response chart for the density data.

**Figure 5(x) Response chart for density data**



Analysis of the response chart revealed that the optimal factors for producing the desired positive paste density of approximately  $4.10 \text{ g/cm}^3$  was to use lead oxide powder with middle free lead content (23 to 25%), middle apparent density ( $1.10$  to  $1.18 \text{ g/cm}^3$  and twenty-four hours old. To check the reproducibility of the results an estimate of the response (density) under the recommended condition ( $A_2B_2C_2$ ) had to be performed. It was compared with the results of a confirmation run. Again the additivity of effects principle was used to derive the estimate of response ("main effects" are significant).

Equation 5(ix)

Estimate of response

$$\begin{aligned}\bar{U} &= \bar{A}_2 + \bar{B}_2 + \bar{C}_2 - 2\bar{T} \\ &= 4.09 + 4.09 + 4.10 - 2(4.10) \\ &= 4.08\end{aligned}$$

Two confirmation runs were performed and the results were compared to the predicted process average result. Table 5(xiii) represents the comparison of the results.

Table 5(xiii) Comparison of the confirmation runs with the predicted process average

Confirmation Run		Predicted Process
Case 1 4.07	Case 2 4.07	Average 4.08

Table 5(xiii)

Analysis of the results revealed that the reproducibility for both cases was very good. Therefore, the experimental results were accepted. If there had been no clear correlation between the estimate of response and the confirmation run under the recommended optimized conditions, the large  $L_{27}$  factorial array would have to be used because significant interaction between factors would have occurred.



STATISTICAL TESTS TO DETERMINE WHETHER PASTE STIFFNESS AND DENSITY ARE SIGNIFICANTLY DIFFERENT WHEN PRODUCED USING EITHER LOW, MIDDLE OR HIGH FREE LEAD

The response charts (Figures 5(ix) and 5(x)) revealed the optimum combination of free lead (factor A), apparent density (factor B) and age (factor C) required to give high paste stiffness and a density of 4.10 g/cm<sup>3</sup>.

Each factor has three specification levels. Level one is top quality specification, level two is middle and level three is bottom. The predicted optimum combination required middle specification free lead, middle specification apparent density and 24 hours old. The confirmation run using the optimum conditions were compared with an estimate of response (derived using a principle known as additivity of effects). The two values were identical and as a result the optimum combination of factors were accepted.

The recommended combination of factor levels produced paste stiffness and density which agreed with the calculated estimates of responses (Section 5.5). However, further statistical tests were carried out to determine if stiffness and density were

significantly different when produced using either the recommended level for a property or the other neglected values (i.e. show that the differences highlighted by the Taguchi method are significant and not just due to normal sample variation).

Two statistical techniques (pooled estimates of standard deviations and T tests) were used and the free lead factor was the property chosen. Although the free lead property was the only factor used for this example, either of the two remaining factors could be used. However, free lead was chosen as the company considered it to be the most important factor affecting paste composition.

### Calculations<sup>23</sup>

#### Investigation of paste density

#### Comparison of factor A<sub>1</sub> with A<sub>2</sub>

The following equations<sup>23</sup> were used to compare free lead level one (factor A<sub>1</sub>) with free lead level two (factor A<sub>2</sub>). The mean for both groups of data were calculated using equation 5 (x).

$$\text{Mean } x = \left\langle \frac{x_i}{n} \right\rangle \quad \text{Equation 5 (x)}$$

Where:  $x_i$  = number of measurements

$n$  = number of samples

$$\bar{x}_{(A1)} = \frac{4.17+4.18+4.17+4.16+4.06+4.08}{6}$$

$$\bar{x}_{(A1)} = 4.14$$

$$\bar{x}_{(A2)} = \frac{4.08+4.09+4.04+4.05+4.13+4.12}{6}$$

$$\bar{x}_{(A2)} = 4.09$$

The standard deviations for both groups of data were calculated using equation 5(xi).

Standard deviation  $S = (x_i - \bar{x})^2/n-1$  Equation 5(xi)

Where:  $n-1$  = number of degrees of freedom

$$S(A_1) = \sqrt{\frac{(4.17-4.14)^2+(4.18-4.14)^2+(4.16-4.14)^2+(4.17-4.14)^2+(4.08-4.14)^2+(4.06-4.14)^2}{5}}$$

$$S(A_1) = 0.05$$

$$S(A_2) = \sqrt{\frac{(4.08-4.09)^2+(4.09-4.09)^2+(4.04-4.09)^2+(4.05-4.09)^2+(4.13-4.09)^2+(4.12-4.09)^2}{5}}$$

$$S(A_2) = 0.03$$

The variance for both groups was calculated by squaring the standard deviations (Equation 5(xii)).

$$\text{Variance } S^2_{(A1)} = (0.05)^2$$

$$S^2_{(A1)} = 0.02$$

Equation 5 (xii)

$$\text{Variance } S^2_{(A2)} = (0.03)^2$$

$$S^2_{(A2)} = 0.0009$$

The next step was to calculate the pooled estimate of standard deviation calculated from two individual standard deviations (Equation 5 (xiii)). The null hypothesis is adopted that using either free lead content has no affect on paste density.

Equation 5(xiii)

$$\text{Pooled estimate } S_2 = \{(n_1-1)S^2 + (n_2-1)S^2\} / (n_1+n_2-2)$$

Where:  $n$  = number of samples

$S^2$  = variance

$$S^2 = (5 \times 0.002 + 5 \times 0.0009) / 10$$

$$\text{Pooled estimate } S = 0.03$$

Having calculated pooled estimate, the T test could be used (Equation 5(xiv)).

$$T = (\bar{x}_1 - \bar{x}_2) / S \sqrt{(1/n_1 + 1/n_2)} \quad \text{Equation 5(xiv)}$$

Where:  $T$  = observed value

$\bar{x}_1$  = mean of sample 1

$\bar{x}_2$  = mean of sample 2

$S$  = pooled estimate

$n_1 + n_2$  = number of readings for each sample

$$T = (4.14 - 4.09) / 0.03 \sqrt{1/6 + 1/6}$$

$$T \text{ (observed value)} = 2.89$$

There are ten degrees of freedom so the critical

value is 2.23( $p = 0.05$ )<sup>23</sup>. The observed value of  $T$  is greater than the critical value, hence the null hypothesis is rejected. If either  $A_1$  (high free lead) or  $A_2$  (middle free lead) is used to produce paste, significantly different densities are obtained.

#### Comparison of factor $A_2$ with $A_3$

The same equations were used to determine the pooled estimate. The observed value of  $T$  (1.73) was found to be less than the critical value of  $T$  (the critical value at  $p = 0.05$  and ten degrees of freedom was 2.23). As the observed value of  $T$  is less than the critical value the null hypothesis is retained (using either free lead content has no effect on density). If either  $A_2$  (middle free lead) or  $A_3$  (low free lead) is used to produce paste, similar densities will be obtained.

#### Investigation of paste stiffness

##### Comparison of factor $A_1$ with $A_2$

The observed value of  $T$  (2.96) was found to be greater than the critical value of 2.23. As the observed value of  $T$  is greater than the critical value the null hypothesis is rejected. If either  $A_1$  (high free lead) or  $A_2$  (middle free lead) is used to

produce paste, a significantly different stiffness will be obtained.

#### Comparison of factor $A_2$ with $A_3$

The observed value of  $T$  (0.42) was found to be less than the critical value of 2.23. As the observed value of  $T$  is less than the critical value the null hypothesis is retained (using either free lead content has no effect on density). If either  $A_2$  (middle free lead) or  $A_3$  (low free lead) is used to produce paste, a similar stiffness will be obtained.

#### Conclusion

The results revealed that for both paste stiffness and density, level two (predicted optimum level) is not significantly different to level three, but level two is significantly different to level one. Although the previous recommendation was that middle specification (level two) free lead should be used, in practice it may not matter if lead oxide with bottom specification (level three) free lead were used. (This allows the company greater flexibility during lead oxide production). However, at no point during paste production could top specification (level one) free lead be used.

The results of the statistical analysis has not affected the overall conclusion for chapter five. Although it has been proven that using either the middle or low specification free lead does not produce paste which has significantly different stiffness and density, it is still my recommendation that the company aim to produce middle specification free lead which was shown to be the preferred condition from the optimisation trials. The results of the statistical analysis will allow the company a degree of flexibility during production. For example, if the company experience problems maintaining free lead content at 25%, they have the option to lower it to 22% without significantly affecting paste composition.

## 5.7

### CONCLUSION

The results of the optimisation tests clearly revealed that variations in lead oxide quality affected both the density and stiffness of freshly mixed pastes.

Analysis of the paste density results revealed a range from 4.03 to 4.18 g/cm<sup>3</sup> which covered the recommended specification range for positive paste. Comparison of the average response values of each lead oxide factor level, revealed that to produce a

positive paste density of  $4.10 \text{ g/cm}^3$  required a free lead content of 23 to 25%, an apparent density of  $1.10$  to  $1.18 \text{ g/cm}^3$  and twenty-four hours old.

To test the result, a confirmation run under the optimal recommended condition was performed. The estimate of response (the paste density) was derived using a principle known as additivity of effects. Two mix runs were performed and the results were compared to the predicted process average results. Analysis of the results revealed that using the recommended combination of lead oxide properties produced a positive paste density of  $4.10 \text{ g/cm}^3$  as predicted by the additivity of effects. Hence the experimental results were accepted.

Analysis of the paste stiffness results revealed a range from 12 to 27 N/mm. No recommended specification range for paste stiffness existed but paste has to be very stiff to enable it to adhere to cast lead alloy grids. The higher the value, the stiffer the paste.

Comparison of the average response values of each lead oxide factor level, revealed that the highest paste stiffness values could be produced using lead oxide which was twenty-four hours old, had a free lead content of 23 to 25% and an apparent density of



1.10 to 1.18 g/cm<sup>3</sup> (this was the same lead oxide property combination which was required to produce the paste density of 4.10 g/cm<sup>3</sup>).

To test this result, a confirmation run under the optimal recommended condition was performed. Two mix runs were again performed and the results were compared to the predicted process average results. Analysis of the results revealed that using the recommended combination of lead oxide properties produced a positive paste stiffness of 29 N/mm as predicted by the additivity of effects. Hence the experimental results were accepted.

Hence the use of fractional factorial design optimisation techniques revealed that paste with high stiffness and a density of 4.10 g/cm<sup>3</sup> required the same quality lead oxide powder.

To consistently produce positive paste with a density of 4.10 g/cm<sup>3</sup> and a stiffness of 29 N/mm requires that the pasting process only uses lead oxide which is twenty-four hours old, has a free lead content of 23 to 25% and an apparent density of 1.10 to 1.18 g/cm<sup>3</sup>. The better understanding of the ball mill process, the reintroduction of the apparent density test, the development of an improved method for measuring free lead and the introduction of an

automatic control system has enabled the ball milling process to be controlled to consistently produce the required lead oxide quality type.

## CHAPTER SIX

### 6.0 CONCLUSION AND BENEFITS TO THE COMPANY

The work accomplished during the Research Project has resulted in considerable benefits for the company. Several of these are qualitative and difficult to put in cost terms. For example, there is considerably improved process knowledge and many company staff now believe in the benefits to be gained by systematic investigative work.

- (i) The factors influencing lead oxide quality were determined. Before the start of the Research Project, lead oxide quality data showed considerable variation. If consistent paste composition was to be achieved, it was necessary to determine the reason for the variations in the quality of freshly produced lead oxide powder. For instance, the property used to assess lead oxide quality is also used to control the ball milling process. Depending on whether quality starts to approach either bottom or top specification levels, the oxide mill operators adjust the setpoint value of a process variable to return quality to the middle specification range.

Tests (Chapters Three and Four) revealed that the factor responsible for the apparent quality variation was experimental error associated with the titration procedure used for determining free lead.

If free lead values cannot be measured accurately, it means that the operators are using false data to control the oxide mill process, therefore making it impossible to produce lead oxide powder with consistent quality.

However, having determined the reason for the previously observed lead oxide quality variations, the company are now in a position to produce lead oxide powder with stable quality.

- (ii) A new experimental procedure for measuring free lead was developed. Free lead is a property of lead oxide powder which is used to assess its quality. Before the start of the Research Project, the experimental procedure used to measure free lead in lead oxide samples involved performing a titration. However, the titration procedure was found to be prone to analytical errors which seriously affected the

accuracy of free lead results.

To be able to continue using the free lead property for the assessment of lead oxide quality, a new experimental procedure for measuring it had to be developed. The experimental procedure was based on the test used throughout the other Companies within the group. It involves dissolving a sample of lead oxide powder in a 1:3 ratio by volume of glacial acetic acid and deionized water solution. The test proved capable of reproducible results. It was therefore introduced as the new experimental procedure for measuring free lead.

(iii) The results of the steady state sensitivity trials provided the information which has led to the development of an automated system for controlling both the production and quality of lead oxide powder (the company have invested £60,000 in purchasing and developing the control system). The control system has ensured that:

(a) Each process variable is controlled to ensure that lead oxide is produced with consistent quality and at a good rate of

production.

- (b) Mechanical features of the oxide mill which have a history of premature failure are continually monitored. The essential monitoring will help with preventative maintenance. This will reduce the oxide mill down time to a minimum.

The projected cost savings for the company have been calculated in terms of oxide mill down time. That is, reduction in monthly budgeted quantities of lead oxide powder, leading to less battery production and hence a decrease in the company's turnover.

The total number of batteries budgeted for 1993/94 is 3.8 million, which works out to be 11,000 batteries per day. In order to produce this number of batteries, the required budgeted rate of lead oxide powder is 4,000,000 kg, which works out to be 11,000 kg per day. Therefore, it can be seen that 1 kg of oxide is required to produce one battery.

However, to actually produce 11,000 kg a

day requires that the mills run at maximum capacity. Also no down time must occur. However, down time is occurring at the average rate of fifteen hours per month. Over a year, the loss in lead oxide production will be 41,220 kg, which corresponds to the company producing approximately 41,220 batteries less than their budgeted total.

Therefore by not eliminating the maintenance down time, a 1.08% reduction in the budgeted production of batteries occurs. This results in a reduction of £216,947 from the company's multimillion pound turnover.

- (iv) The use of fractional factorial design experiments predicted the combination of lead oxide properties (free lead, apparent density and age) which could produce a positive paste density of  $4.10 \text{ g/cm}^3$ . This was verified by performing an experimental confirmation run using the predicted optimum lead oxide quality, i.e. free lead 22 to 25%, apparent density  $1.10$  to  $1.18 \text{ g/cm}^3$  and age twenty-four hours. The confirmation run agreed with the predicted value calculated from the additivity of

effects.

The introduction of the lead oxide ball mill automated control system has enabled the company to stabilise the quality of freshly produced lead oxide powder. The process variables will be set up and controlled to ensure that the lead oxide which is used for pasting has the optimum combination of free lead, apparent density and age.

Having determined that an optimum combination of lead oxide properties is required, to consistently produce a positive paste density of  $4.10 \text{ g/cm}^3$ , the company may introduce more stringent production control techniques. If this is continually achieved the company will be able to produce positive electrodes which provide batteries with improved lifetime and performance characteristics. Therefore, securing the company's present world market share of sealed lead acid battery sales.



## CHAPTER SEVEN

### 7.0 RECOMMENDATIONS FOR FURTHER RESEARCH

The initial requirements for the company's lead/sulphuric acid batteries were to have good lifetime and performance properties. The main applications for these batteries being security systems, emergency backup and uninterrupted power systems (UPS). However, many potential customers have approached the company requesting lead/sulphuric acid batteries which possess excellent cycling lifetime. Cycling lifetime refers to the number of times (cycles) a battery can be charged and discharged before becoming exhausted. These batteries would be used for applications involving high rates of charge/discharge cycles. For example, powered golf trolleys and telecommunication activities. The present applications which the batteries are used for (standby power use) do not require the electrodes to possess good cyclic lifetime properties. Batteries for standby power use only require to be able to last approximately 200 charge/discharge cycles whereas cyclic batteries have to be able to last over 300 charge/discharge cycles.

Therefore the recommendation for the next area of research will be to investigate how to produce

lead/sulphuric acid batteries with extended cyclic lifetime properties. The company believe that achieving cyclic lifetime ability for sealed lead/sulphuric acid batteries depends on the composition of freshly produced positive paste. The new area of research is therefore a direct follow-on from the effect of lead oxide powder on positive paste composition.

It is believed that the cyclic lifetime of the positive plate is largely determined by the efficiency of the setting or cementation process of positive pasted grids in the curing ovens (see Chapter One, Section 1.2.3). The chemical reaction is referred to as hydrosetting. The porosity of freshly mixed positive paste is mainly dependent on the quantity of water left after mixing. To retain this porosity in the finished battery plate (electrode), shrinkage must be kept to a minimum. Porosity has a direct influence on the cycling lifetime of positive electrodes. Conditions in the curing oven are set to stimulate growth of crystalline compounds which form a rigid interlocking fibrous type of matrix. Curing ovens are held at 85% relative humidity to retard the evaporation of water while the compounds are forming. The chemical reaction which occurs in the positive plate is exothermic and the temperature rises appreciably

(oxidation of free lead contributes the majority of heat). At 50°C to 60°C (ideal temperature rise) the main product is hydrated tribasic lead sulphate ( $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ ). Achieving the ideal temperature enables excellent lead alloy grid paste bonds to be formed which provides positive electrodes with excellent cycle lifetime properties. If positive plate temperature rises too much, tetra basic lead sulphate ( $4\text{PbO} \cdot \text{PbSO}_4$ ) is formed which hinders the cyclic lifetime property of positive pasted plates and also poor lead alloy grid paste bonds are formed which further effects the cyclic lifetime ability.

#### 7.1

##### THE KEY AREAS TO BE INVESTIGATED

Both the required positive plate porosity level and correct hydrosetting reaction temperature have to be consistently achieved if positive electrodes with excellent cyclic lifetime properties are to be produced. The factor which is assumed to influence both the porosity of freshly mixed pastes and the temperature rise during the hydrosetting reaction is again lead oxide quality.

The apparent density is believed to affect the water retention in freshly mixed pastes. Apparent density measurements are an indication of lead oxide particle size and water molecules are trapped between the

various sized particles. If large particles of lead oxide powder are present, there are bigger spaces between the particles and as a result more water will be retained, whereas if small lead oxide particles are present, less water will be retained as there is less space between the particles. Hence the particle sizes of lead oxide powder are affecting positive plate porosity and therefore influencing cyclic lifetime ability.

The free lead content is believed to affect the temperature of the hydrosetting reaction. High levels of free lead could be generating too high a temperature, hence leading to the formation of tetrabasic sulphate and poor grid paste bonds. This condition would seriously affect the cyclic lifetime properties of positive electrodes. If lead oxide powder for paste production contained very low levels of free lead, a much lower temperature would be obtained and as a result poor grid paste bonds would be achieved.

It is therefore important that optimum levels for both apparent density and free lead be achieved if the required porosity, grid paste attachment and tribasic sulphate be formed for positive electrodes which are to be used in applications where excellent cyclic lifetime performance is required.

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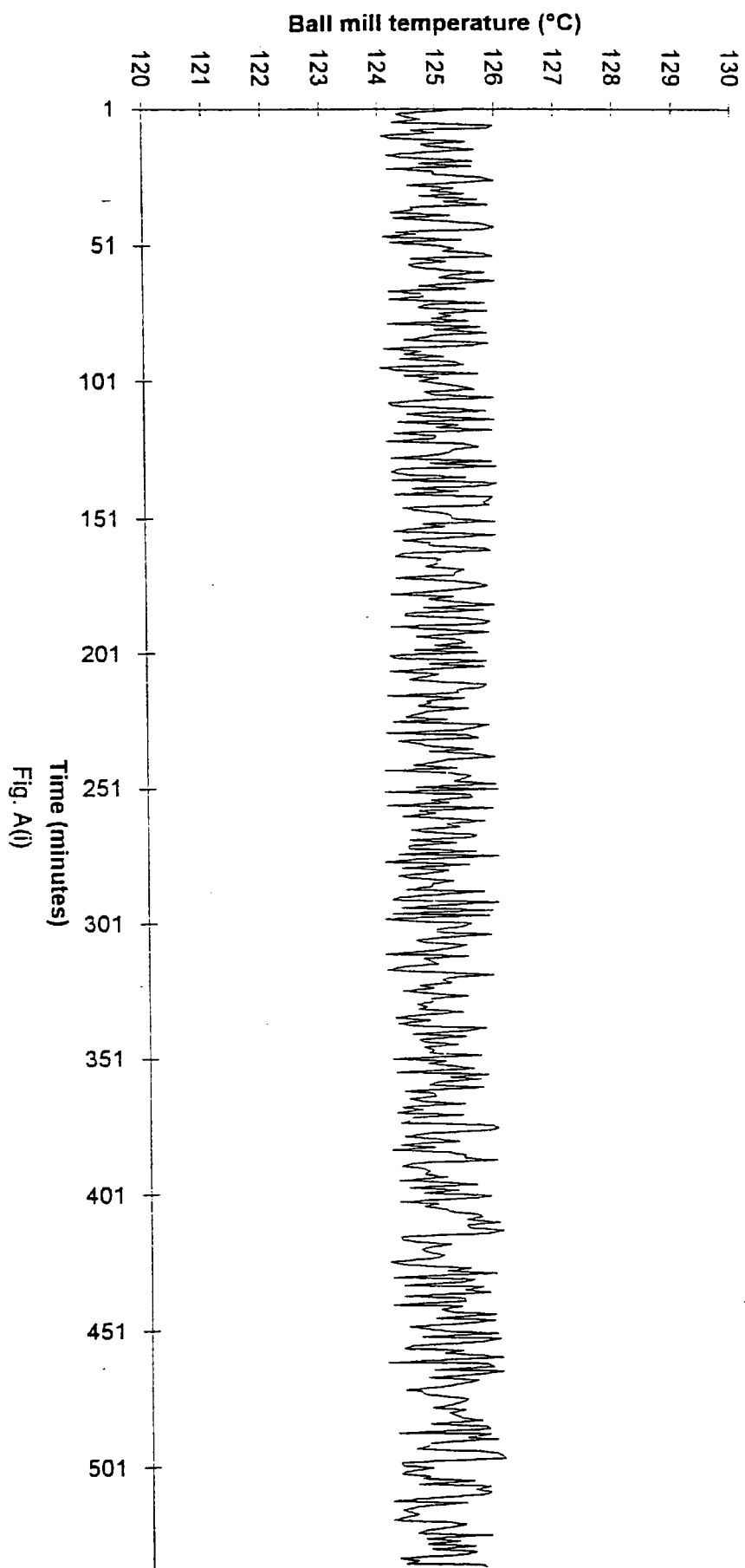


## APPENDIX

Table A(i) Results of particle size determinations using a laser sizer

Sample number	Percentage of particles <5 micrometres	Range (%)	Percentage of particles 5 to 50 micrometres	Range (%)	Percentage of particles >50 micrometres	Range (%)
1	12 55 30	12 to 55	72 42 15	15 to 72	16 3 55	3 to 55
2	30 50 10	10 to 50	60 20 15	15 to 60	10 30 75	10 to 75
3	8 60 21	8 to 60	13 25 75	13 to 75	79 15 4	4 to 79
4	17 50 5	5 to 50	40 25 90	25 to 90	43 25 5	5 to 43
5	11 60 25	11 to 60	16 30 50	16 to 50	73 10 25	10 to 73
6	5 24 45	5 to 45	60 32 49	32 to 60	35 44 6	6 to 44
7	16 29 5	5 to 29	67 30 80	30 to 80	17 41 15	17 to 41
8	12 29 30	12 to 30	70 49 30	30 to 70	18 22 40	18 to 40
9	30 18 10	10 to 30	60 40 30	30 to 60	10 42 60	10 to 60
10	8 32 19	8 to 32	20 50 79	20 to 79	72 18 2	2 to 72
11	5 15 40	5 to 40	60 15 40	15 to 60	35 70 20	20 to 70
12	60 30 15	15 to 60	30 45 80	30 to 80	10 25 5	5 to 25
13	29 9 50	9 to 50	59 31 40	31 to 59	12 60 20	12 to 60
14	16 5 52	5 to 52	62 40 42	40 to 62	22 55 6	6 to 55
15	2 45 62	2 to 62	57 35 30	30 to 57	41 20 8	8 to 41
16	18 4 34	4 to 34	61 43 50	43 to 61	21 53 16	16 to 53
17	6 10 5	5 to 10	86 72 55	55 to 86	8 18 40	8 to 40
18	55 10 8	8 to 55	5 72 90	5 to 90	40 18 2	2 to 40
19	60 15 7	7 to 60	10 80 43	10 to 80	30 5 50	5 to 50
20	19 5 45	5 to 45	71 15 33	15 to 71	10 80 22	10 to 80
21	20 40 9	9 to 40	65 22 48	22 to 65	15 38 43	15 to 43
22	15 32 5	15 to 32	10 40 75	10 to 75	75 28 20	20 to 75
23	2 33 65	2 to 65	41 49 30	30 to 49	57 17 5	5 to 57
24	11 29 5	5 to 29	69 22 60	22 to 69	20 49 35	20 to 49
25	44 10 20	10 to 44	32 80 15	15 to 80	22 10 65	10 to 65

Table A(i)



**Figure A (i) Profile of ball mill temperature during the airflow steady state sensitivity trial**

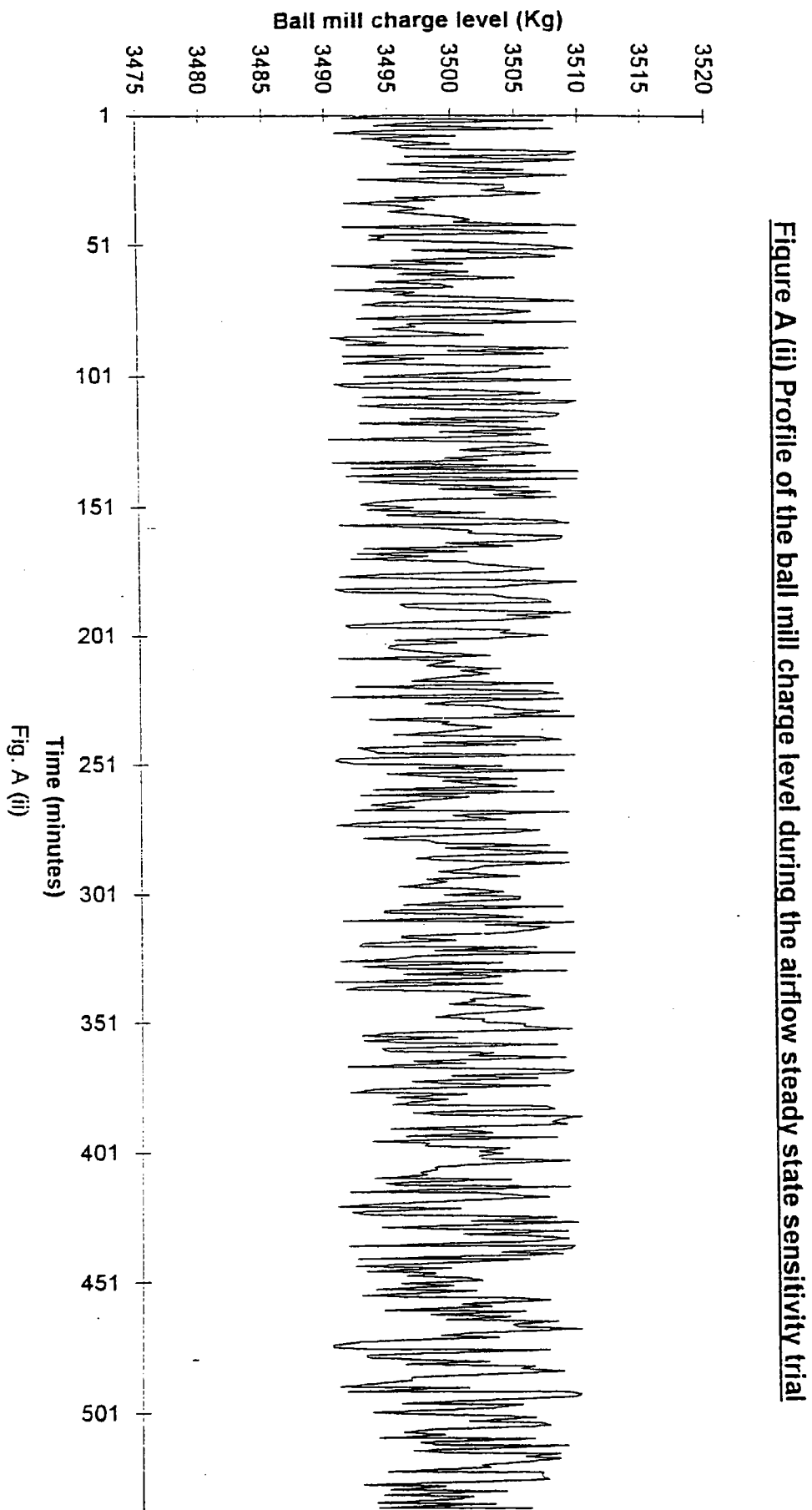


Figure A (iii) Profile of relative humidity of air entering the ball mill during the airflow steady state sensitivity trial

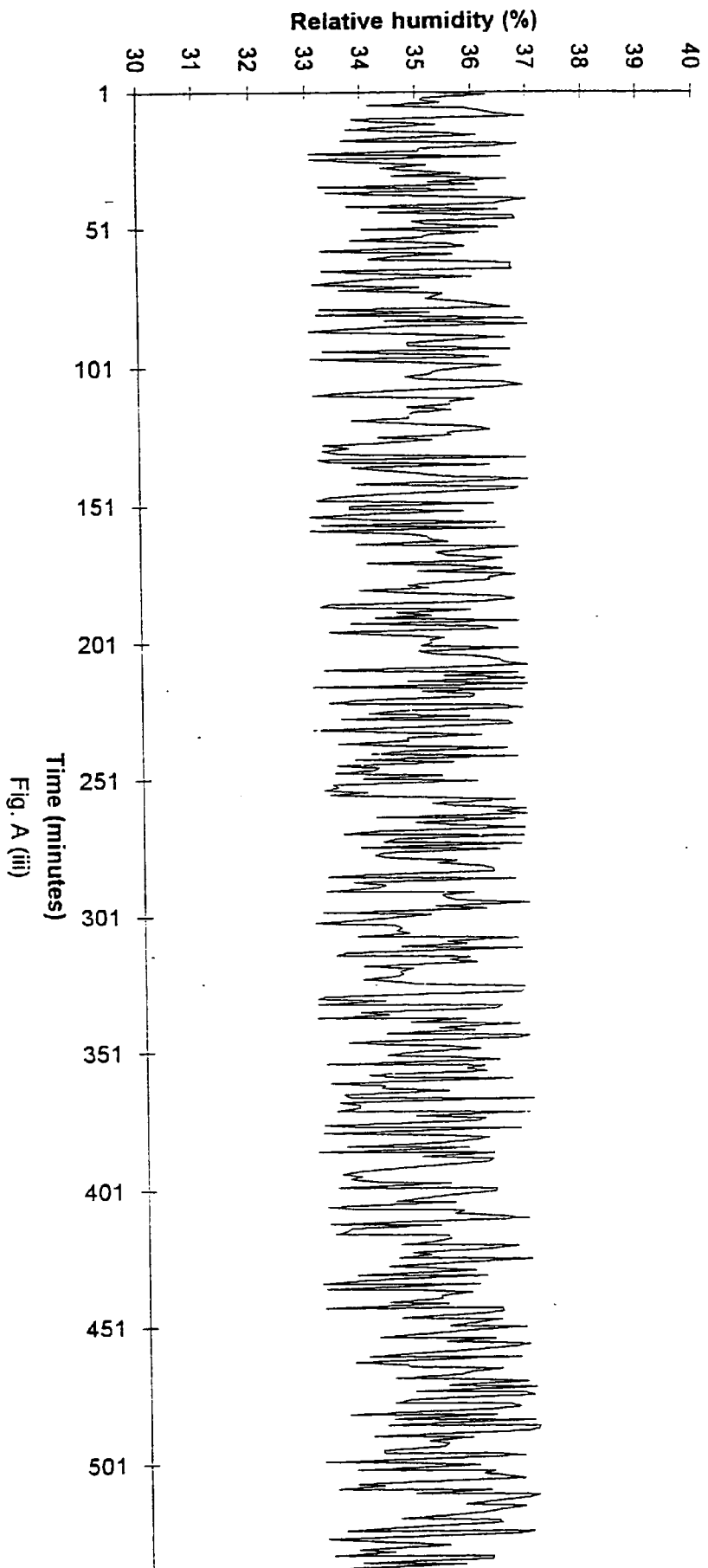
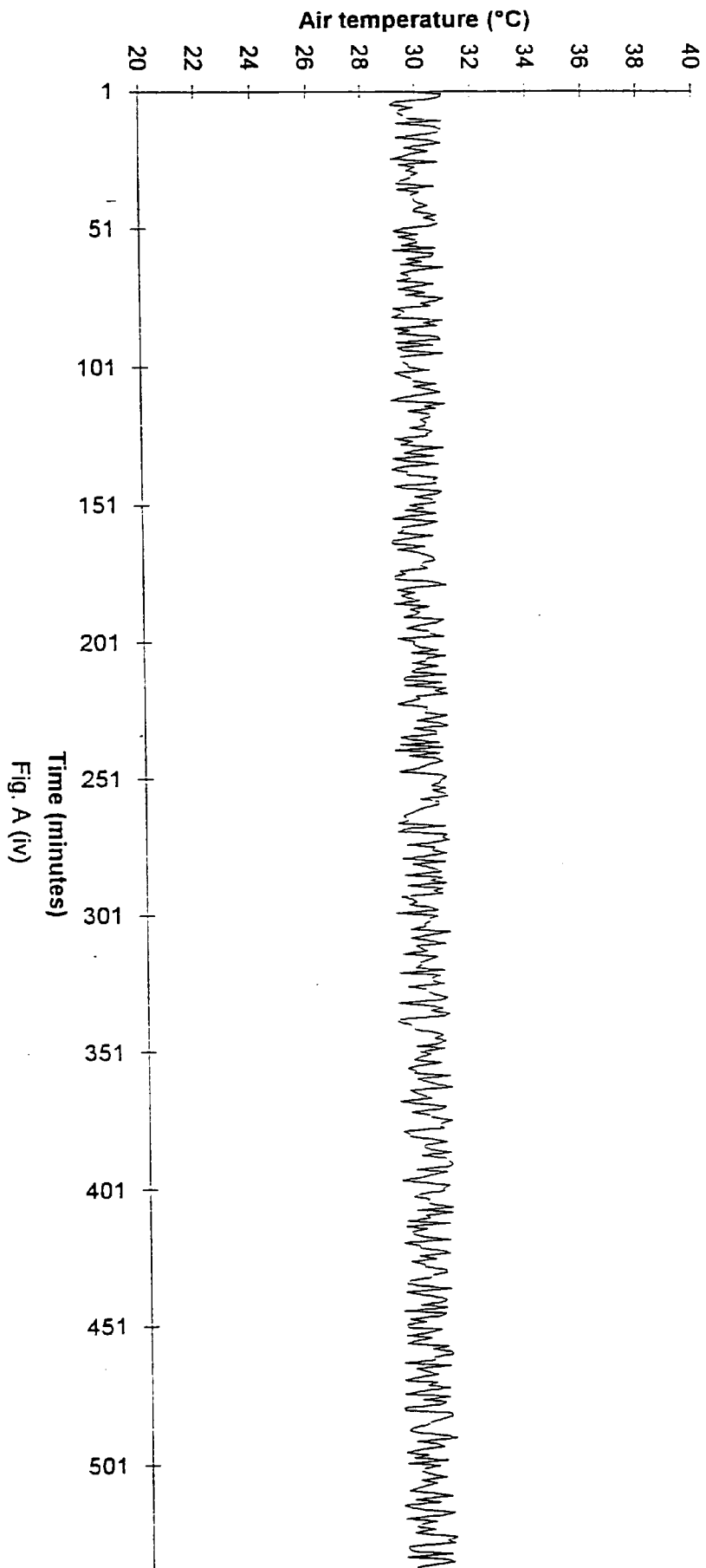


Figure A (iv) Profile of temperature of air entering the ball mill during the airflow steady state sensitivity trial



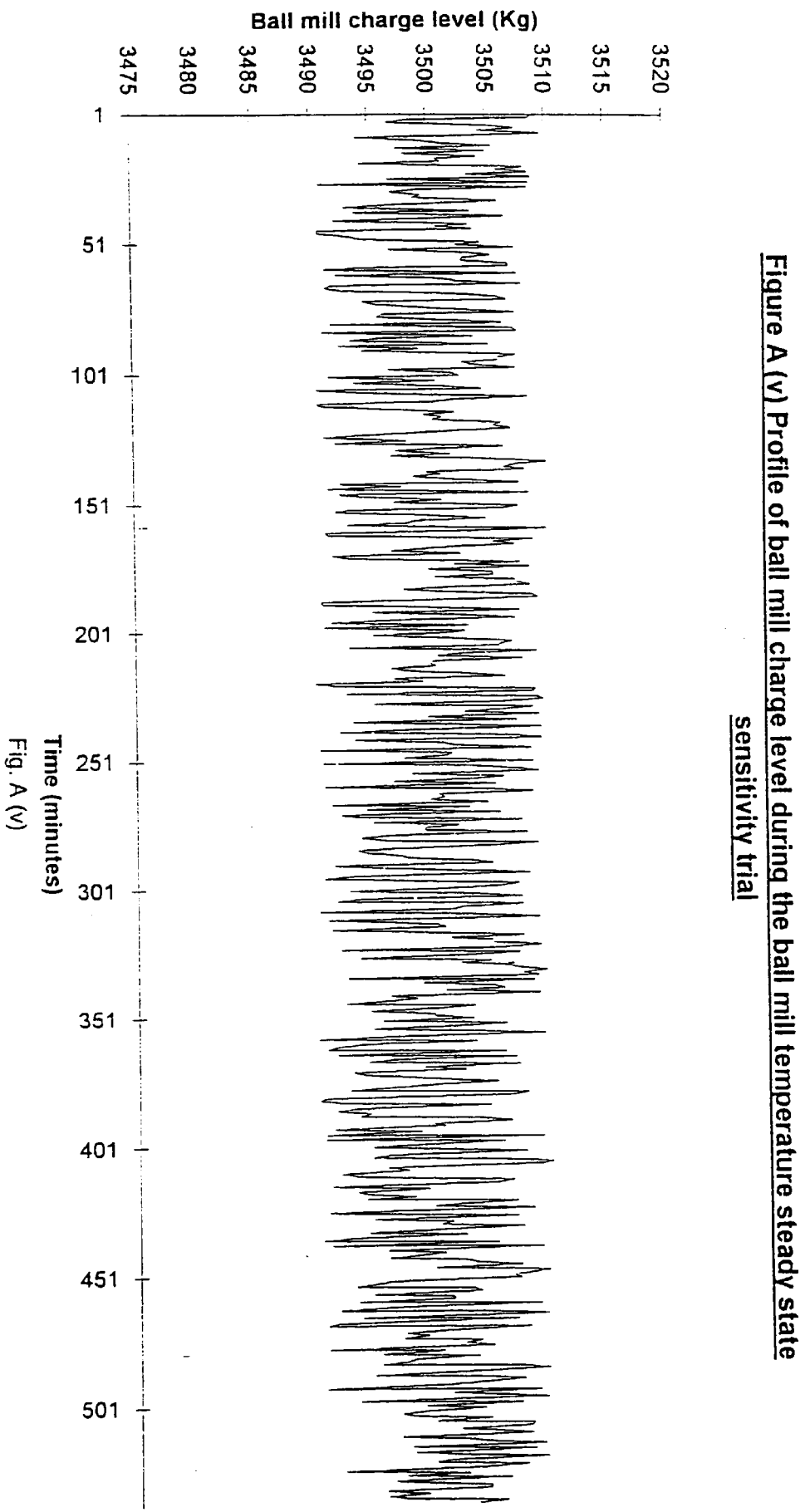


Figure A (vi) Profile of relative humidity of air entering the ball mill during the ball mill temperature steady state sensitivity trial

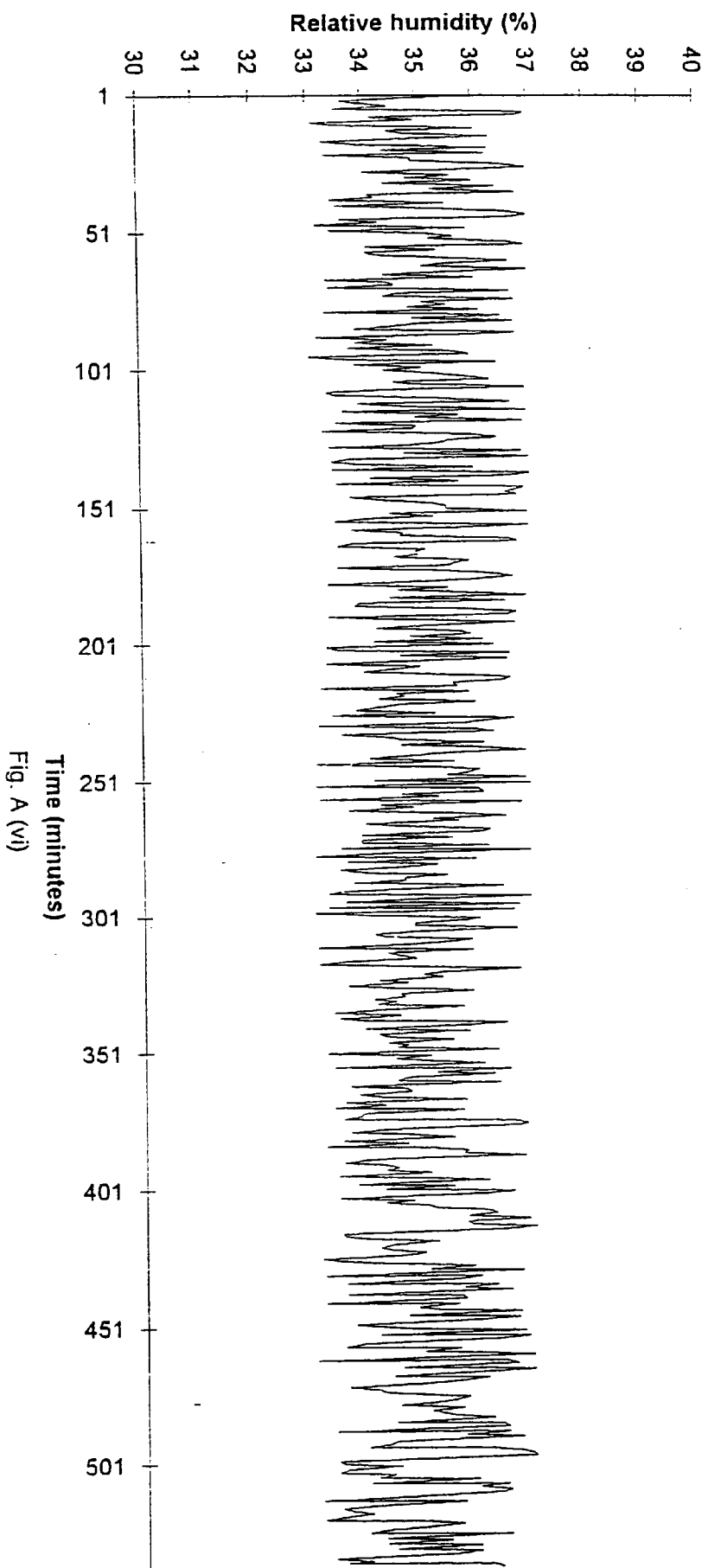
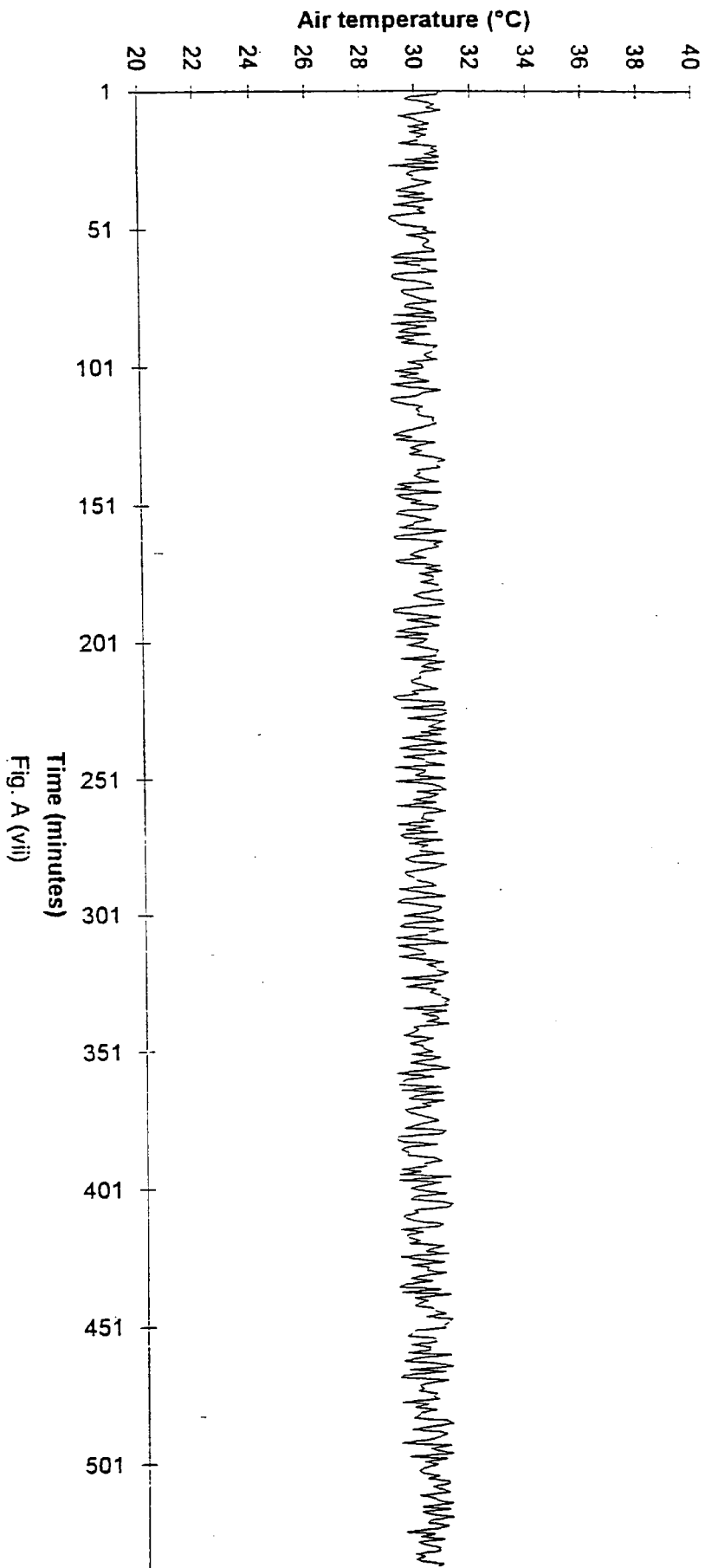




Figure A (vii) Profile of temperature of air entering the ball mill during the ball mill temperature steady state sensitivity trial



Time (minutes)  
Fig. A (vii)

Figure A (viii) Profile of the ball mill temperature during the ball mill charge level steady state sensitivity trial

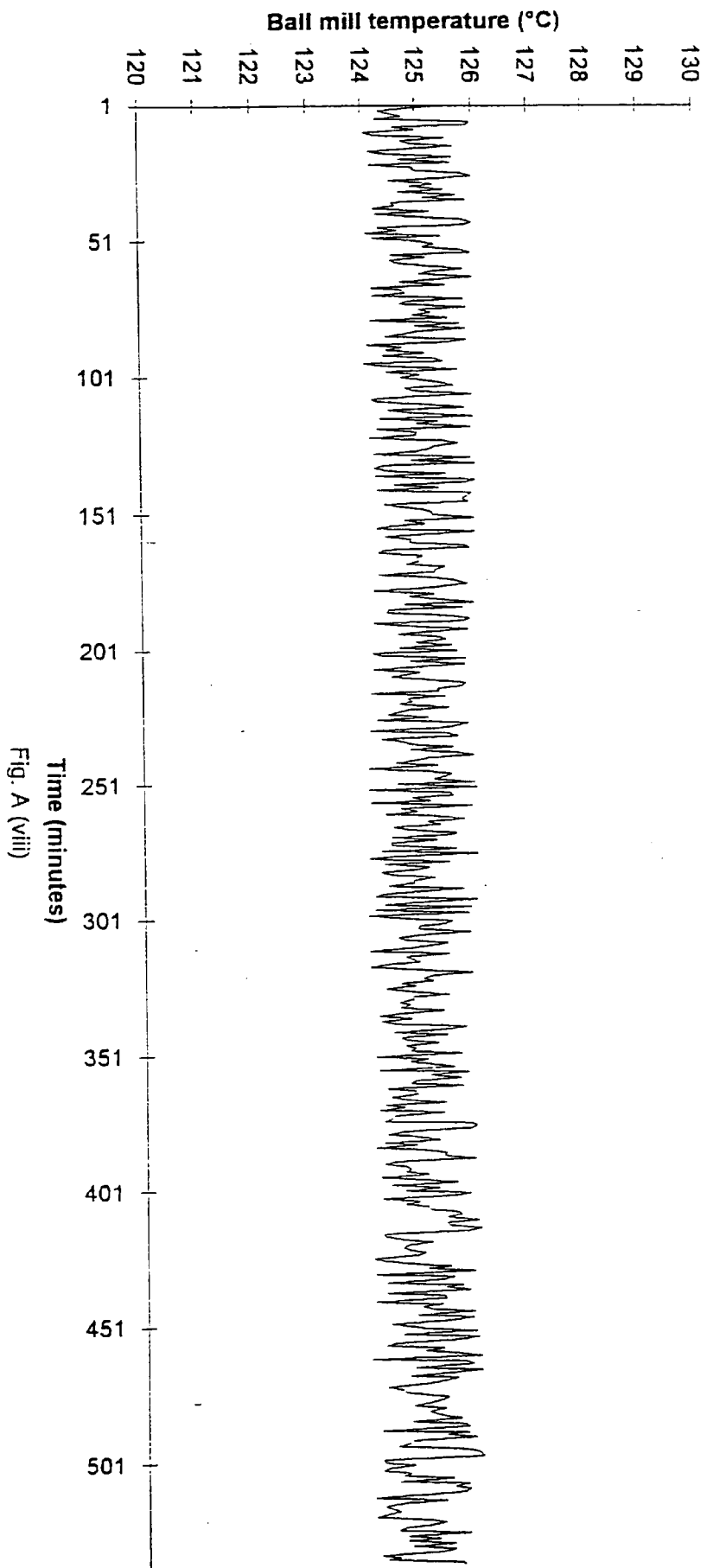
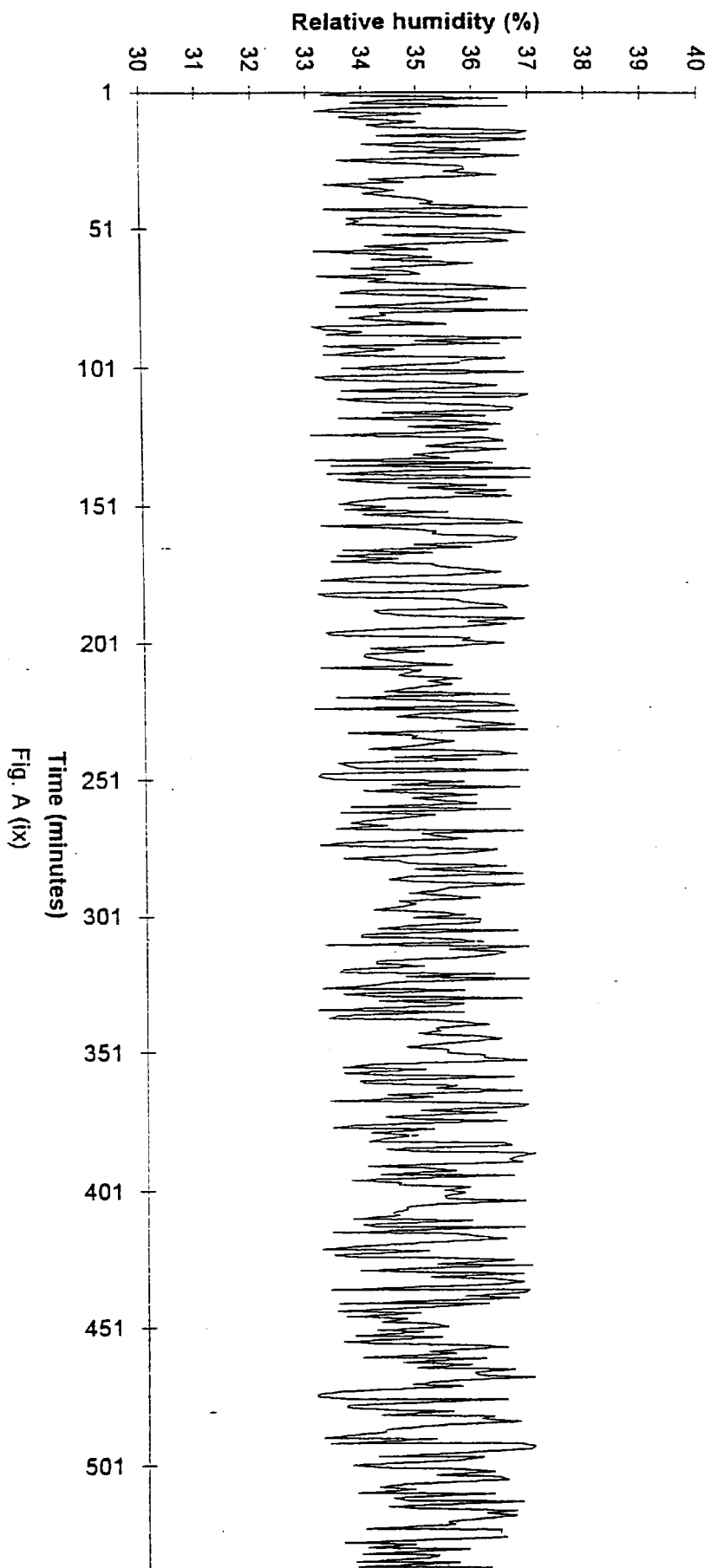


Fig. A (viii)

Figure A (ix) Profile of relative humidity of air entering the ball mill during the ball mill level steady state sensitivity trial



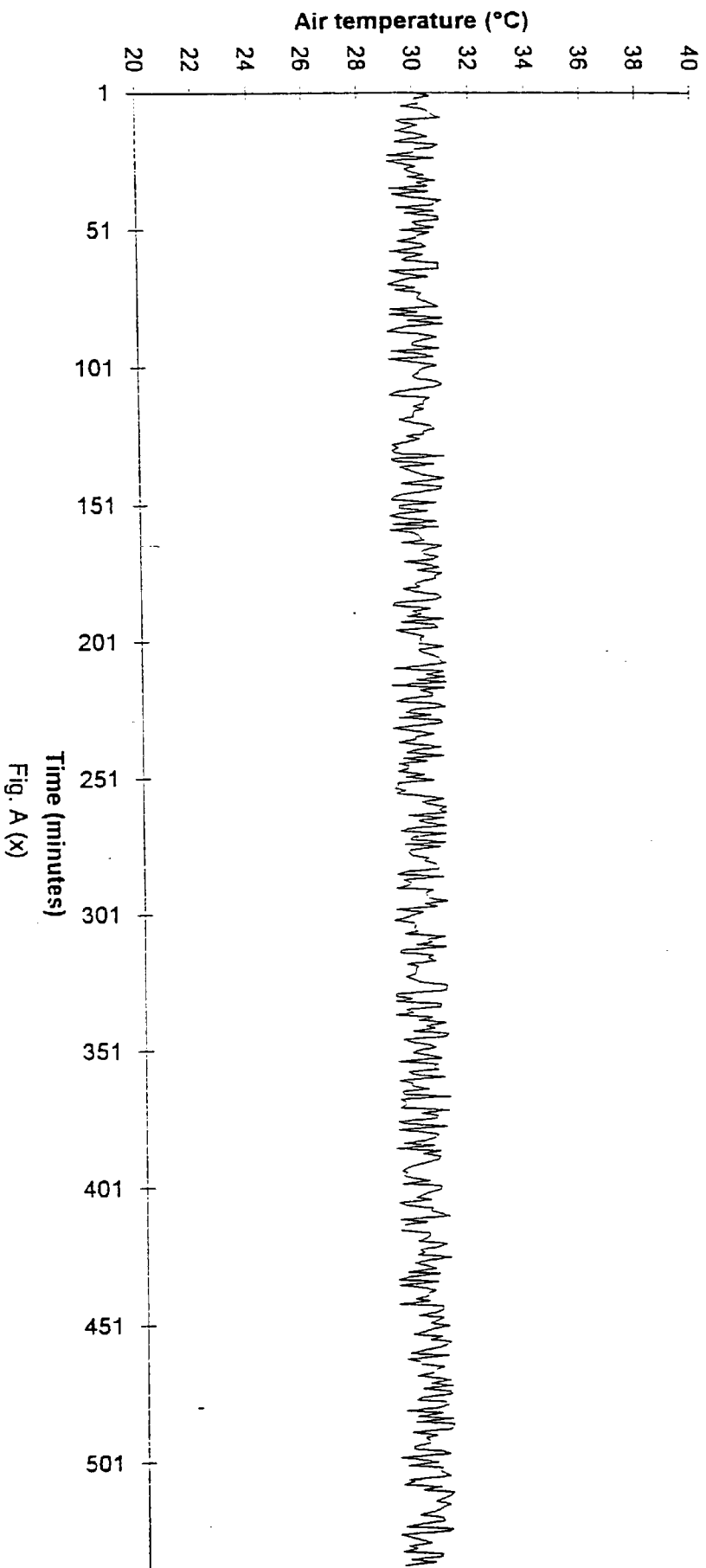


Figure A (x) Profile of temperature of air entering the ball mill during the ball mill charge level steady state sensitivity trial

Figure A (xi) Profile of the airflow through the oxide mill during the ball mill charge level steady state sensitivity trial

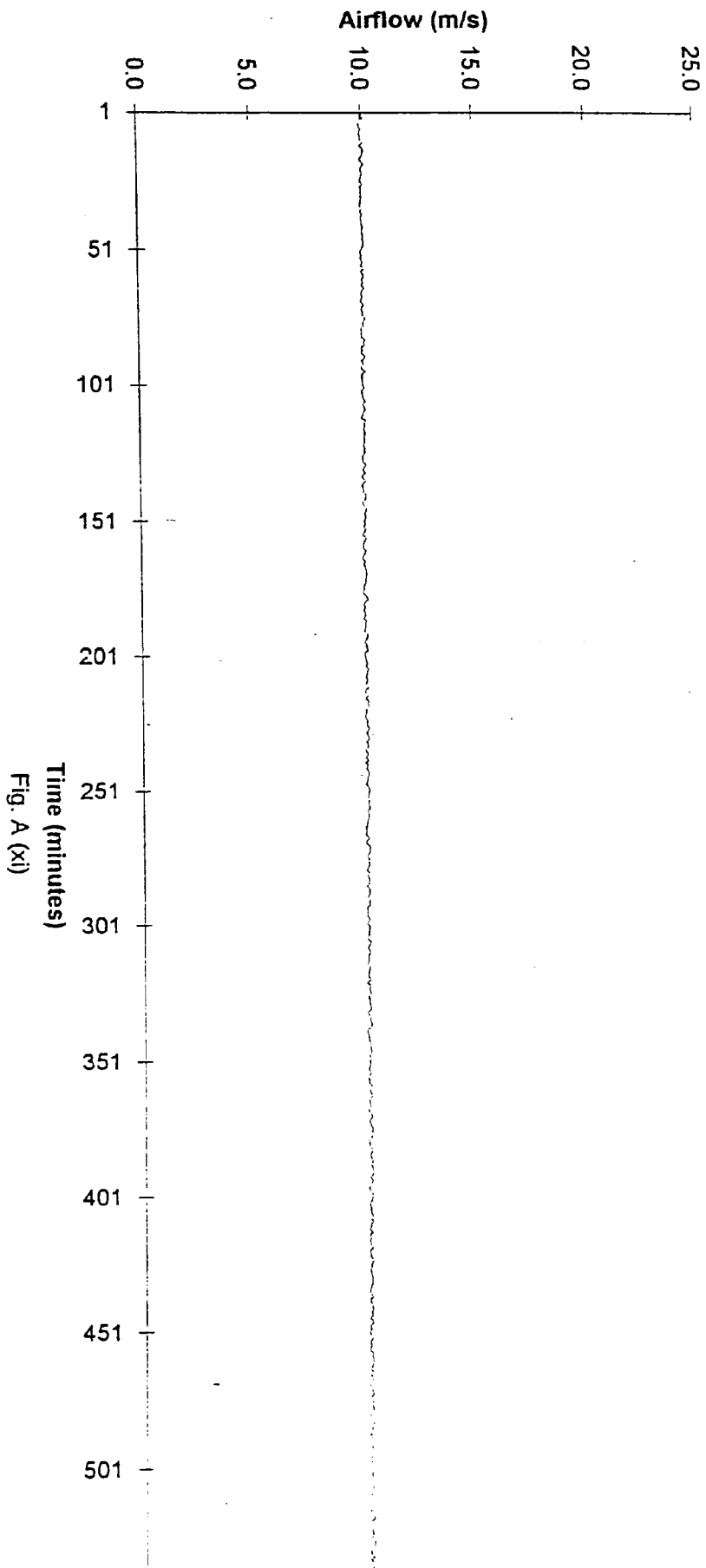
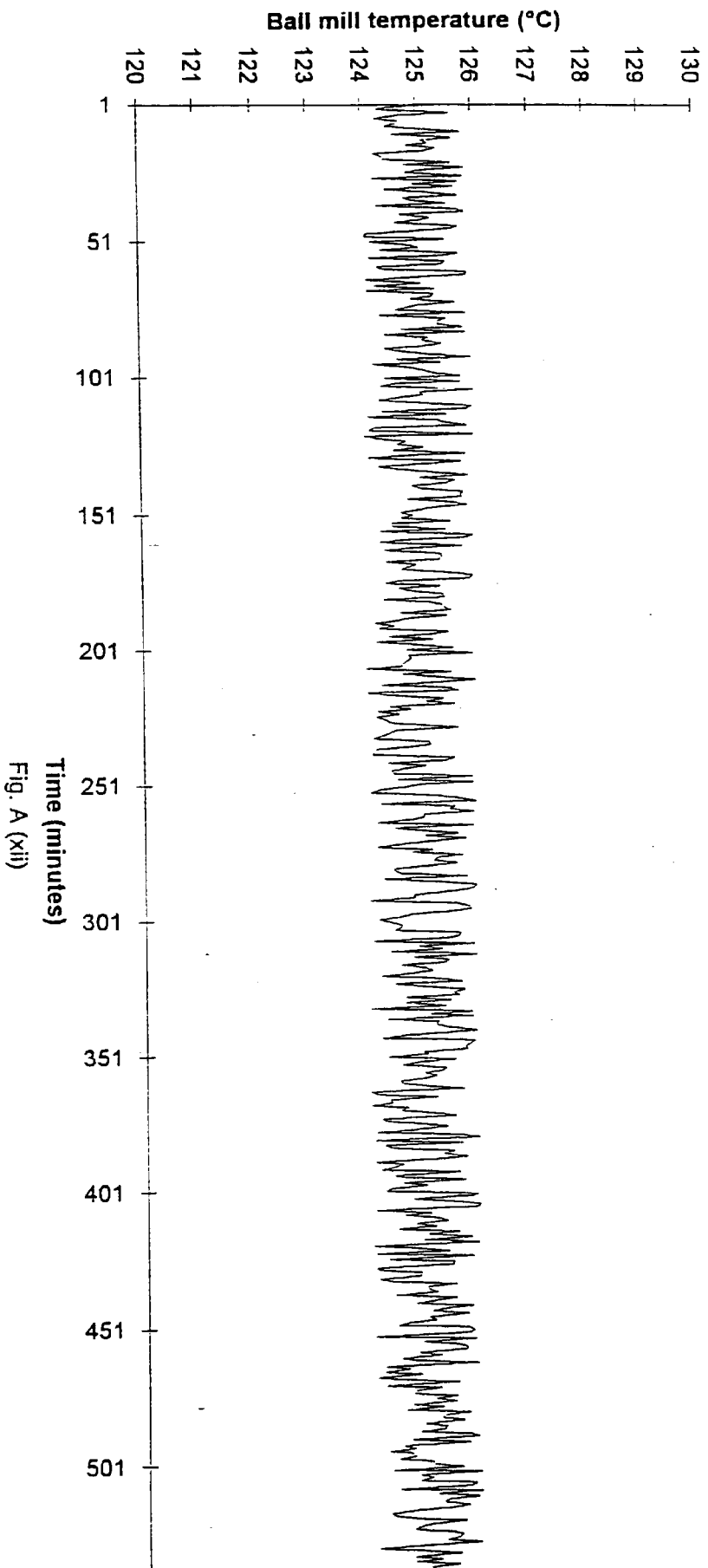


Figure A (xii) Profile of the ball mill temperature during the relative humidity steady state sensitivity trial



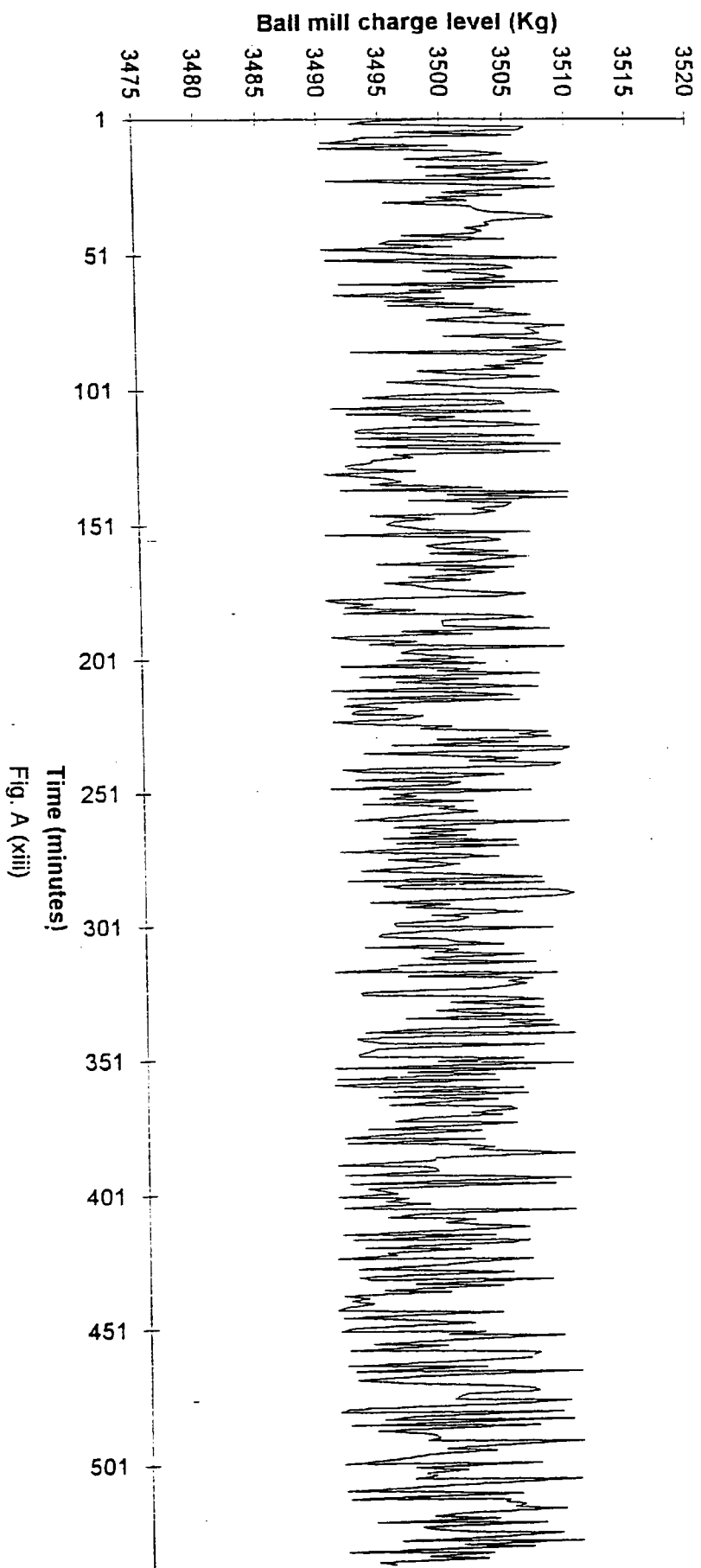
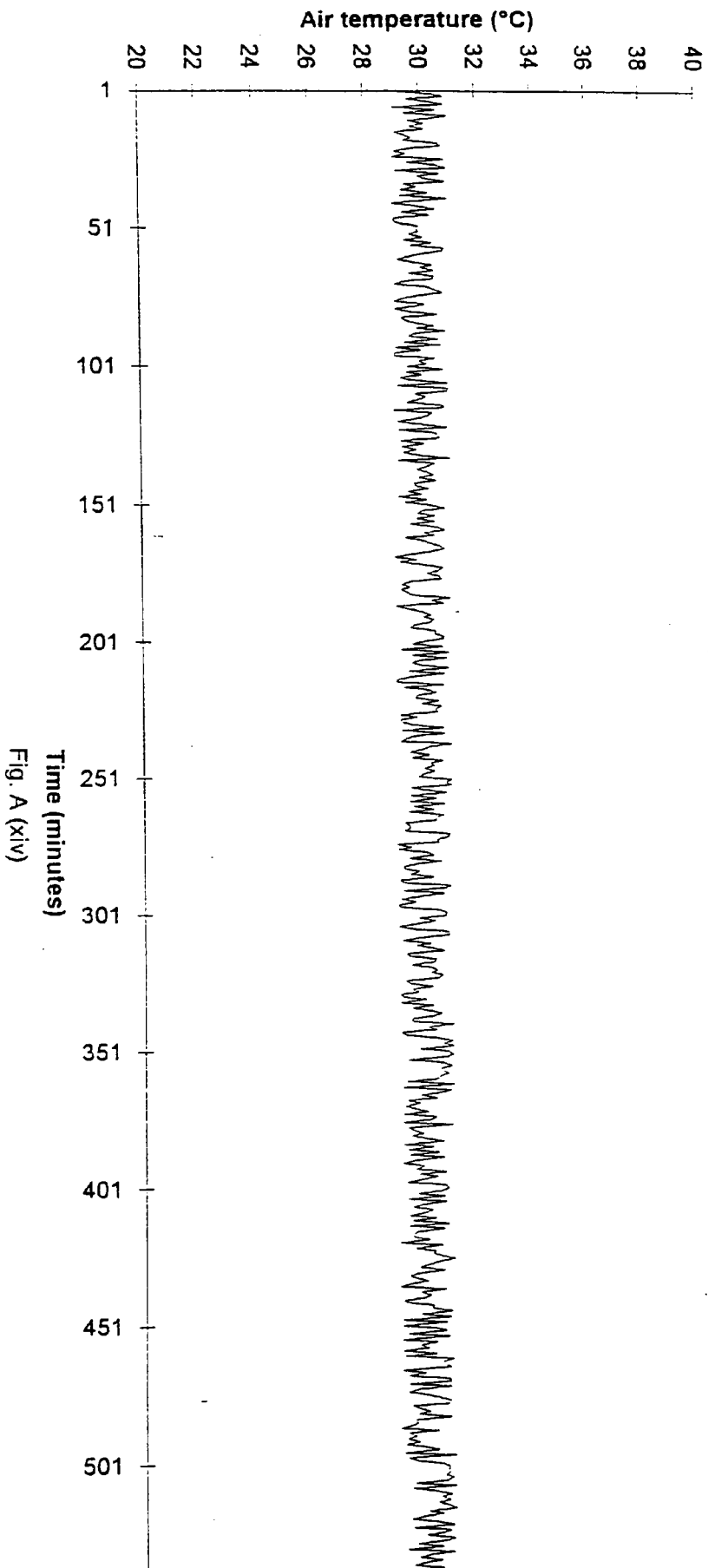
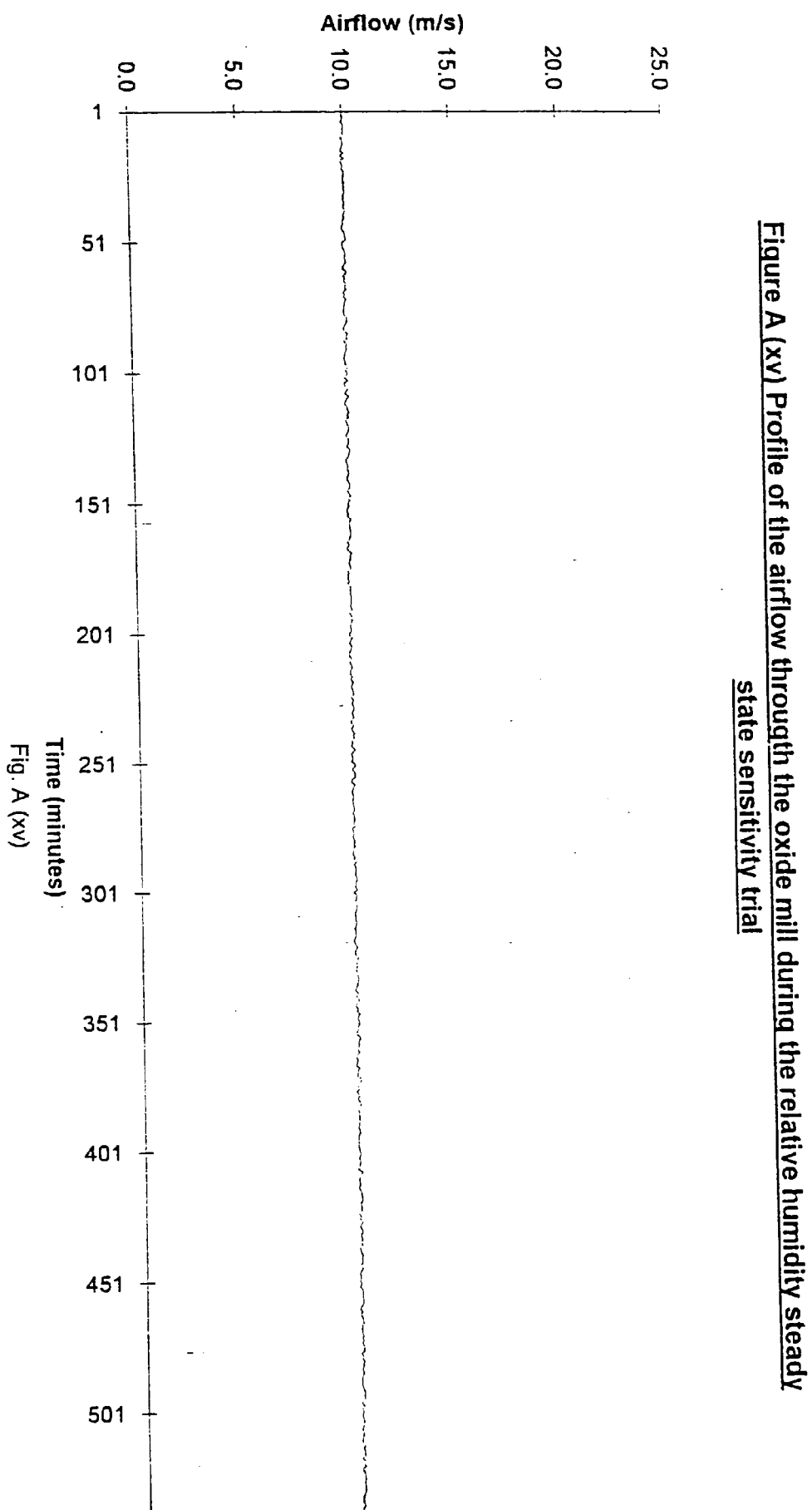


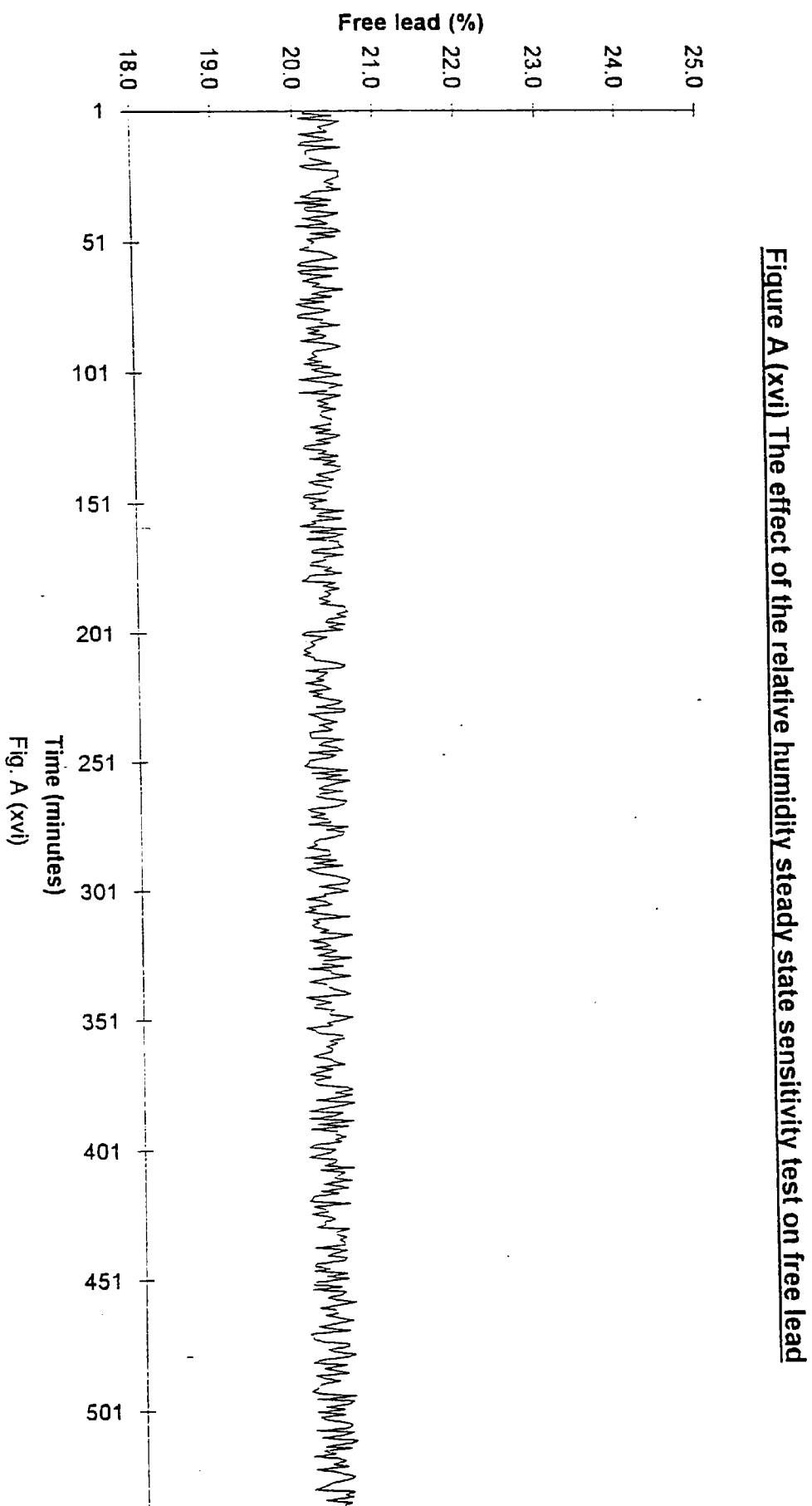
Figure A (xiii) Profile of the ball mill charge level during the relative humidity steady state sensitivity trial

**Figure A (xiv) Profile of temperature of air entering the ball mill during the relative humidity steady state sensitivity trial**

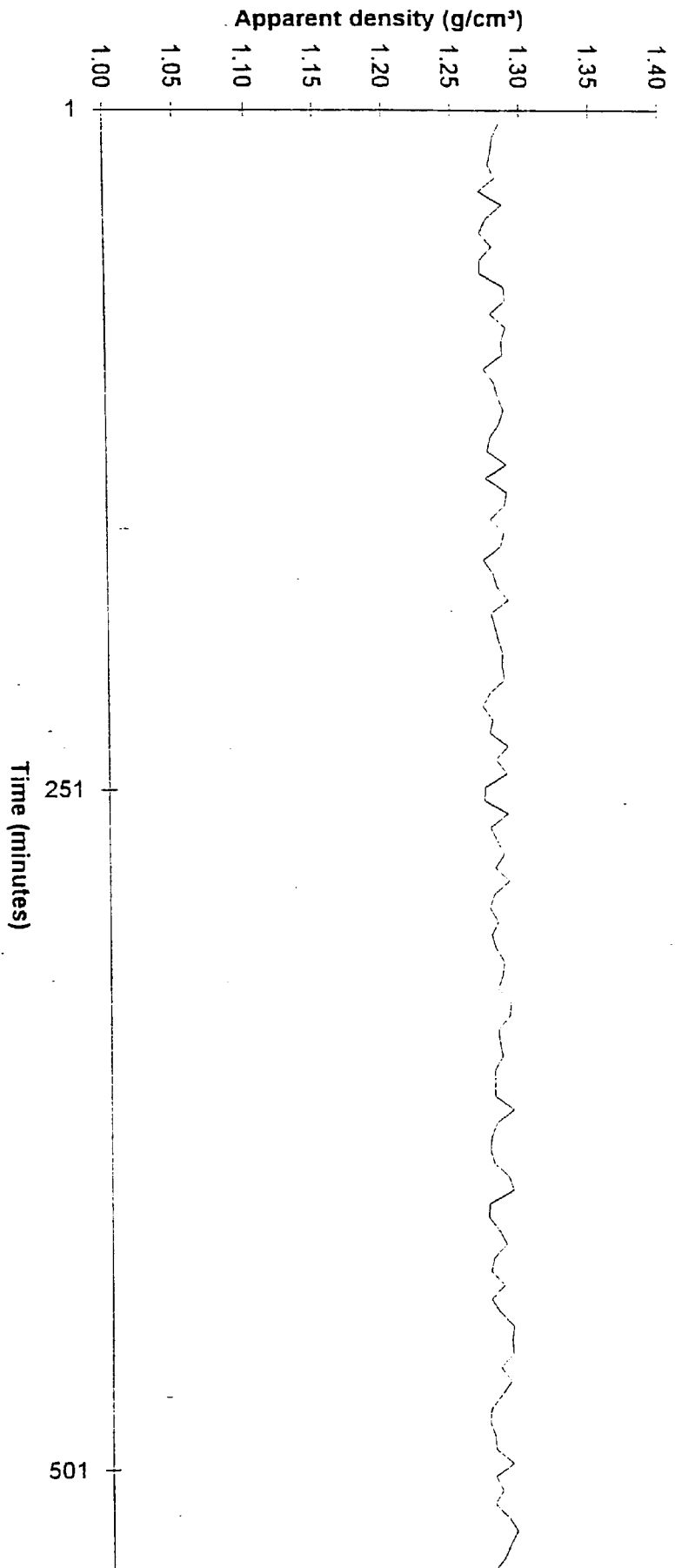








**Figure A (xvii) The effect of the relative humidity steady state sensitivity test on apparent density**



**Time (minutes)**  
**Fig. A (xvii)**

Figure A (xviii) The effect of the relative humidity steady state sensitivity test on lead oxide rate of production

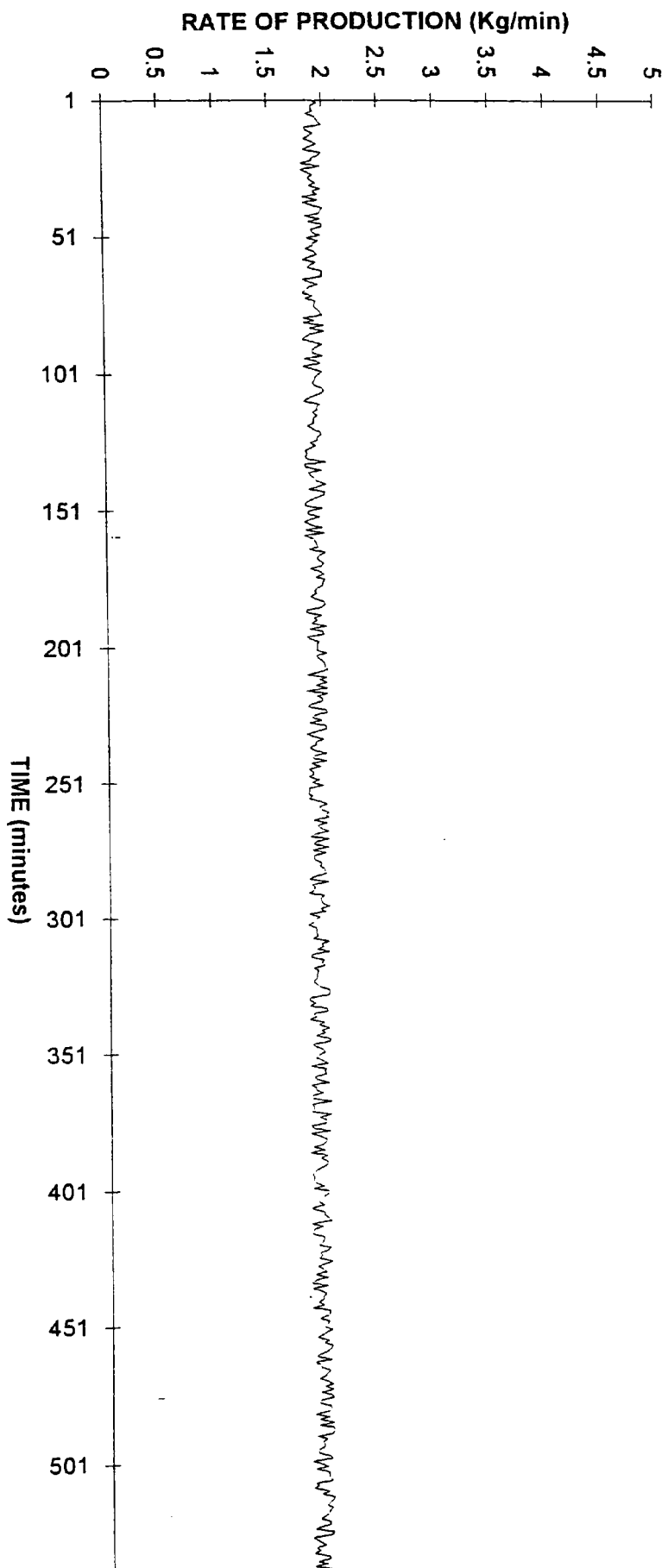


Fig. A (xviii)

Figure A (xix) Profile of the ball mill temperature during the air temperature steady state sensitivity trial

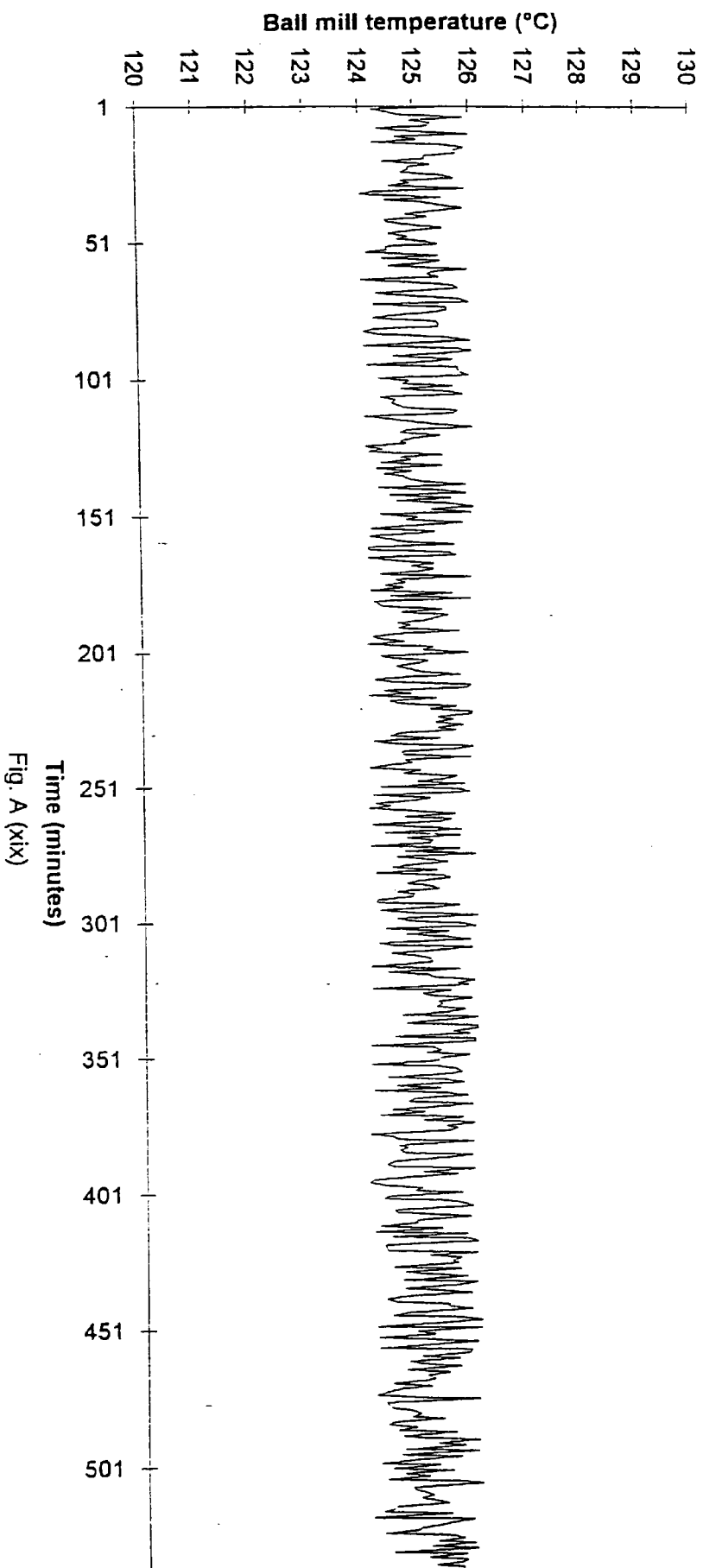


Fig. A (xix)

Figure A (xx) Profile of the ball mill charge level during the air temperature steady state sensitivity trial

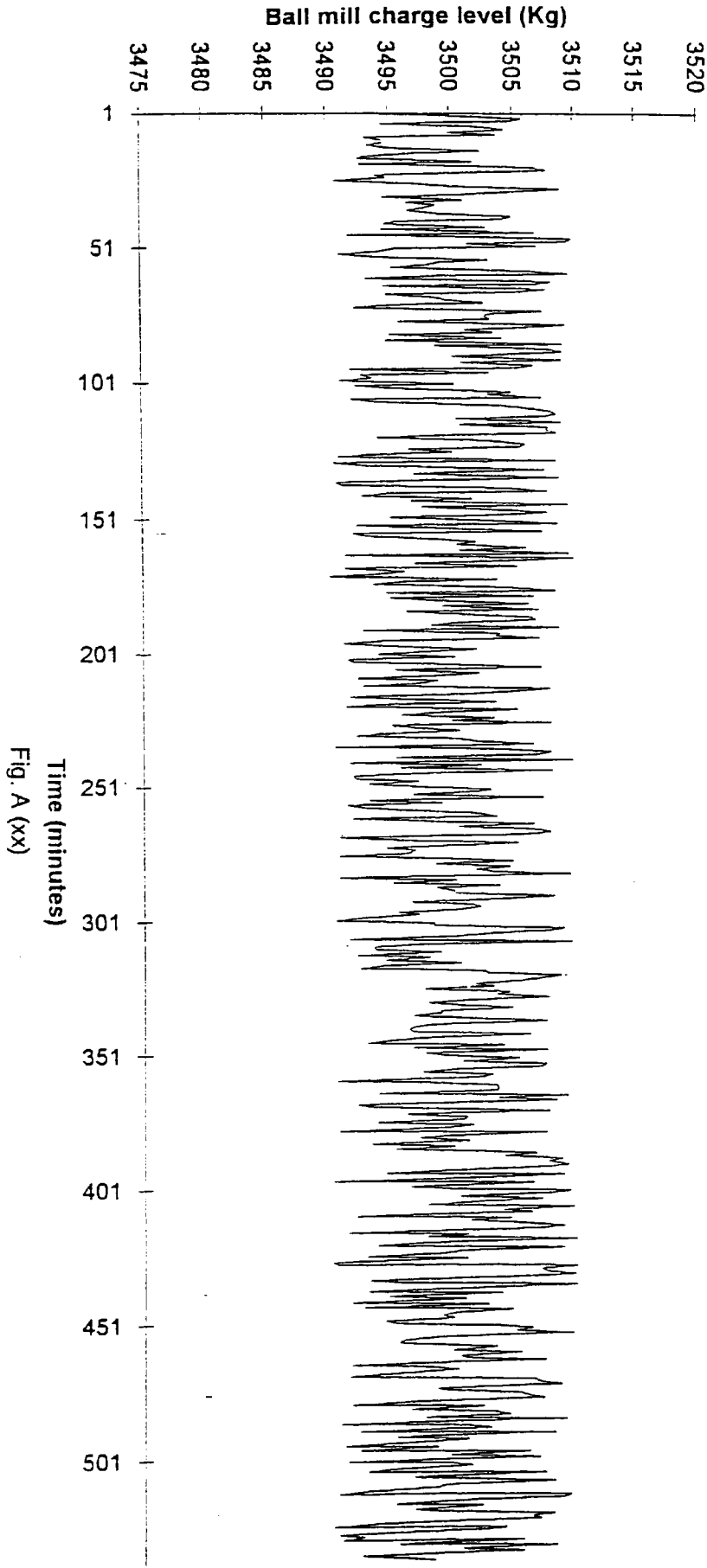


Figure A (xxi) Profile of the airflow through the oxide mill during the air temperature steady state sensitivity trial

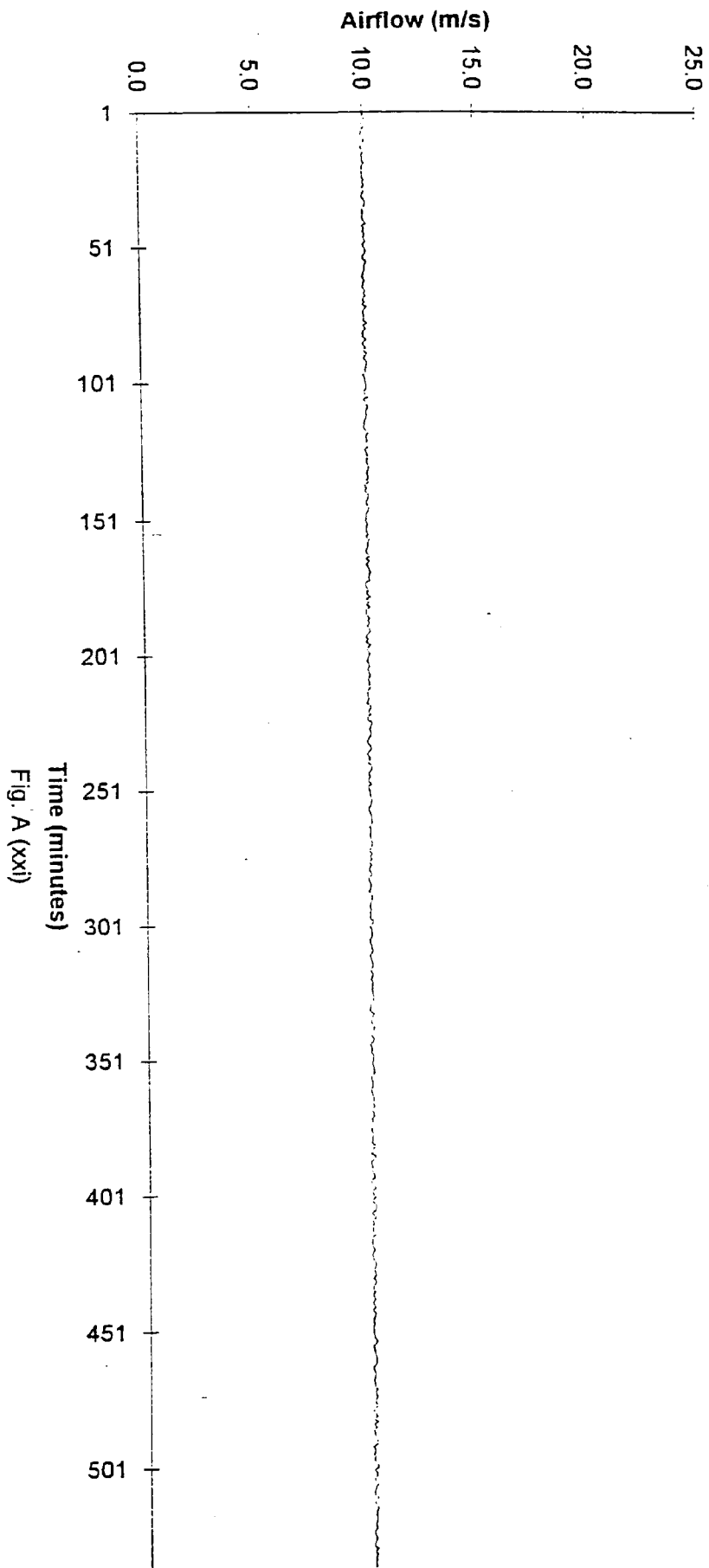
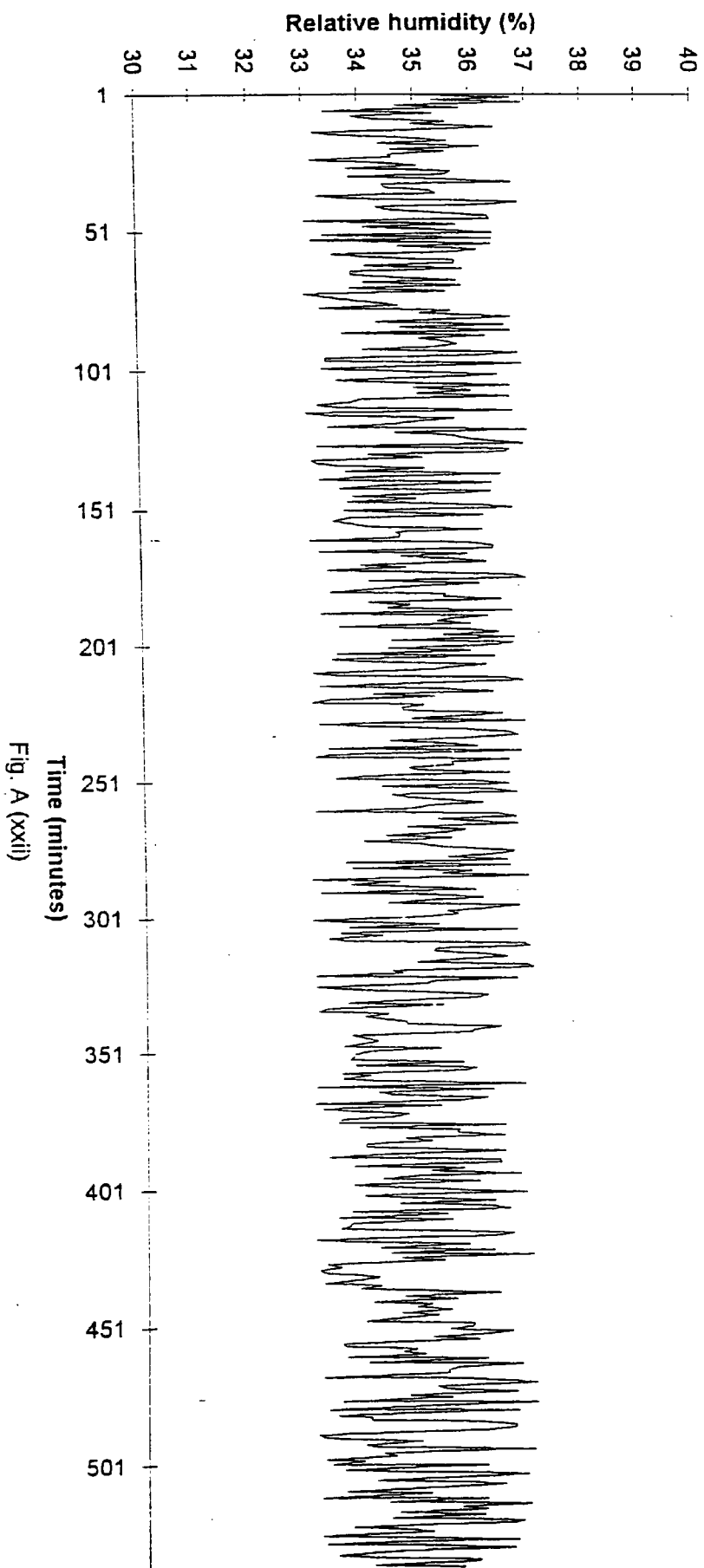
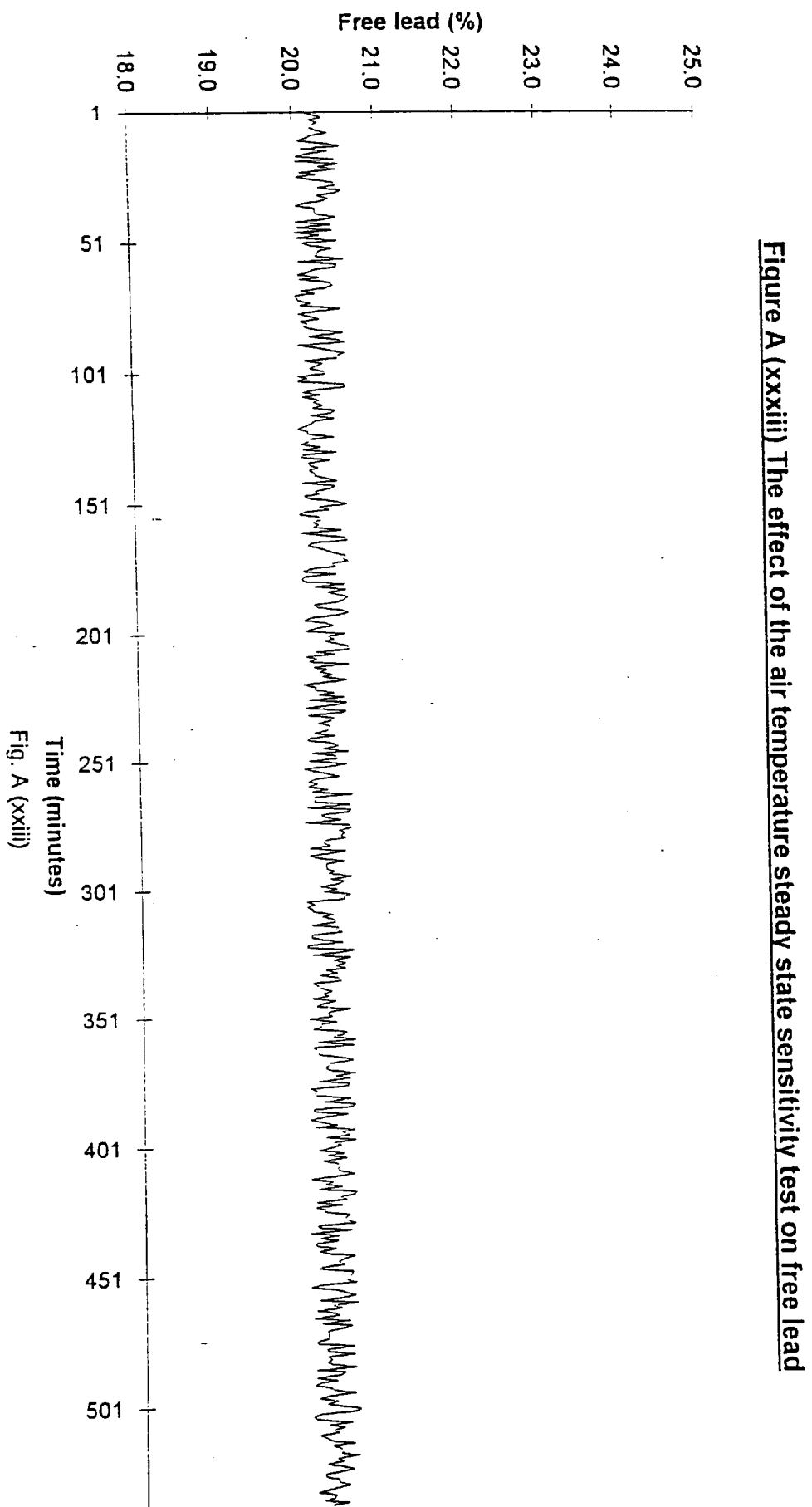


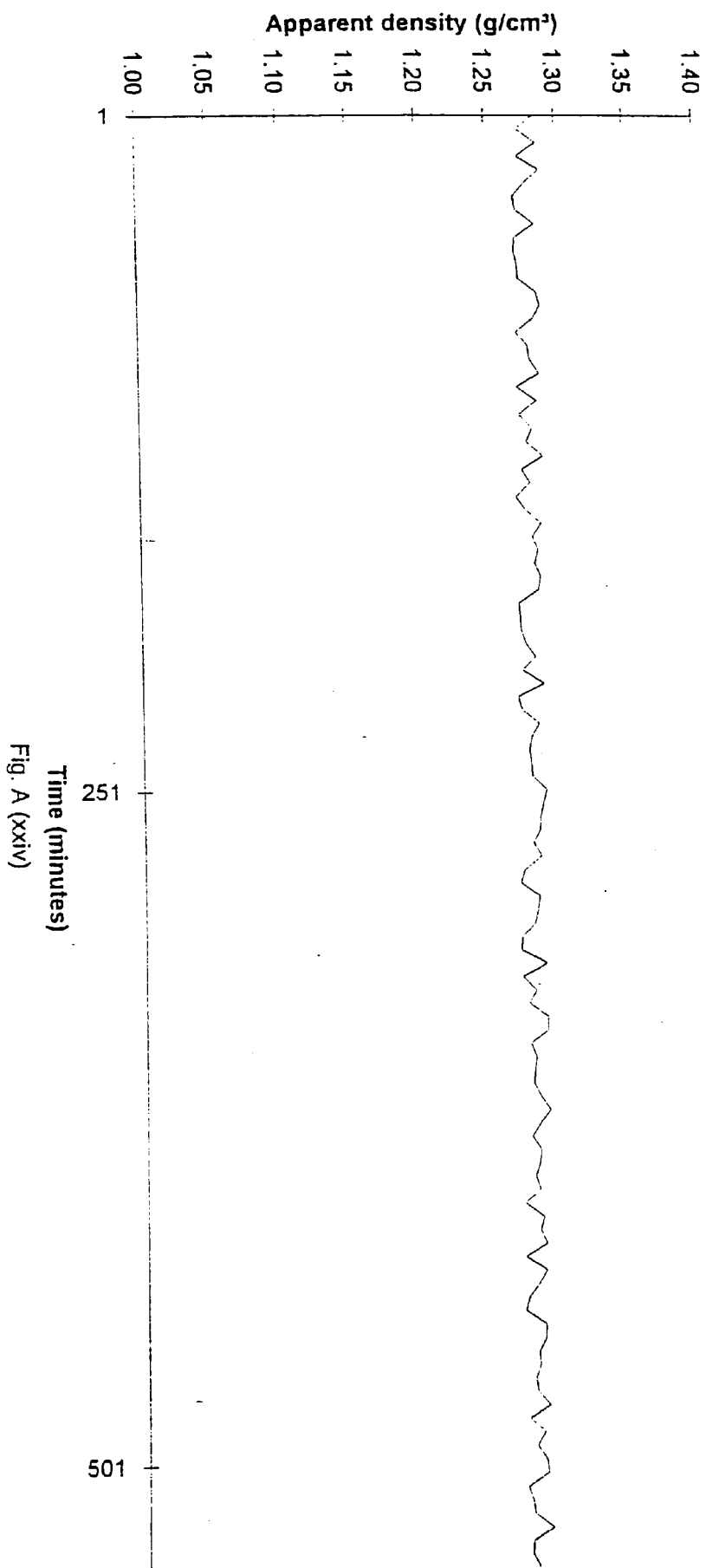
Figure A (xxii) Profile of relative humidity of air entering the ball mill during the air temperature steady state sensitivity trial







**Figure A (xxiv) The effect of the air temperature steady state sensitivity test on apparent density**



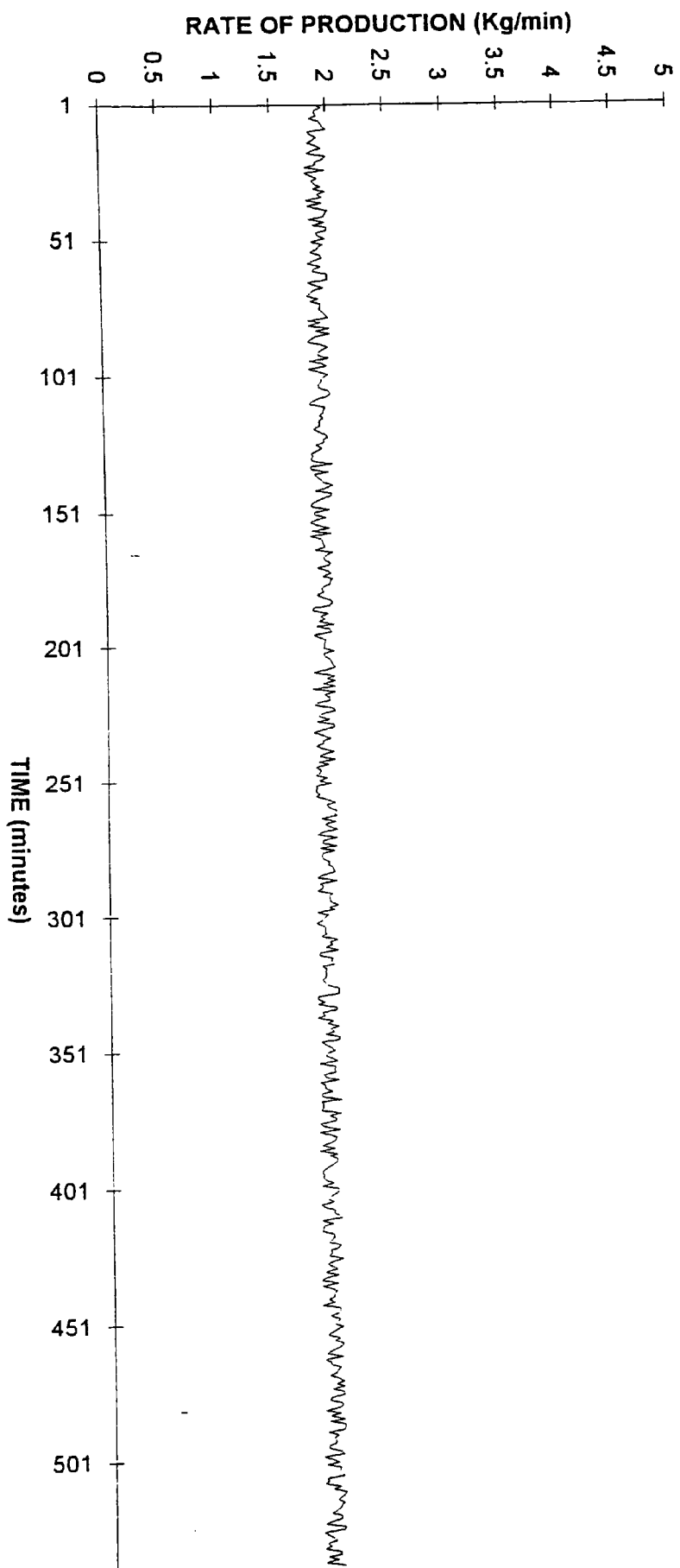


Figure A (xxv) The effect of the air temperature steady state sensitivity test on lead oxide rate of production